

Reactor Handbook: Materials

Volume 4



SELECTED REFERENCE MATERIAL
UNITED STATES ATOMIC ENERGY PROGRAM

1955

Reactor Handbook: Materials



SELECTED REFERENCE MATERIAL

UNITED STATES ATOMIC ENERGY PROGRAM



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Reactor Handbook: Materials



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**SELECTED REFERENCE MATERIAL
ON ATOMIC ENERGY**

- VOLUME ONE Research Reactors**
- VOLUME TWO Reactor Handbook: Physics**
- VOLUME THREE Reactor Handbook: Engineering**
- VOLUME FOUR Reactor Handbook: Materials**
- VOLUME FIVE Neutron Cross Sections**
- VOLUME SIX Chemical Processing and Equipment**
- VOLUME SEVEN Eight-year Isotope Summary**
- VOLUME EIGHT Information Sources**

VOLUME FOUR

Reactor Handbook: Materials

UNITED STATES OF AMERICA

GENEVA: AUGUST 1955

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Foreword

Interchange of scientific and technical knowledge will greatly facilitate the work of the scientists and engineers whose skills will be devoted to the future development of the peaceful uses of atomic energy.

The United States has made available to the world's scientific community a large body of such data. In honor of this historic Conference and to stimulate further exploration and development of the beneficial applications of nuclear energy, the United States Atomic Energy Commission has prepared this special collection of technical data for the use of the delegates and the nations represented.

The purpose of this collection is to provide information concerning the ways that we have found in which fissionable materials can be put to work in nuclear reactors for research purposes and for the production of power and radioisotopes.

It is our sincere hope that this material will be of practical value to the men and women of science and engineering in whose hands the great power of the atom is becoming a benign force for world peace.

A handwritten signature in black ink, reading "Lewis L. Strauss". The signature is written in a cursive, flowing style.

Chairman, U.S. Atomic Energy Commission

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Acknowledgment

This series of volumes was sponsored by the United States Atomic Energy Commission for presentation by the United States of America to the countries represented at the International Conference on Peaceful Uses of Atomic Energy.

The organizations which contributed material presented in these volumes are:

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THE REACTOR HANDBOOK

VOLUME 3 MATERIALS

SECTION 1 GENERAL PROPERTIES

DECLASSIFIED EDITION

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FOREWORD

With the rapid maturity of reactor technology and its growing application to industrial power reactors, there has developed an urgent need for a comprehensive and critical compilation of nuclear engineering data. At the request of Dr. L. R. Hafstad, Director of Reactor Development, and in accord with an over-all program for the organization and consolidation of AEC-developed technical information, the Commission's Technical Information Service has issued this Reactor Handbook for convenient reference use by scientists and engineers engaged on AEC reactor projects.

The material presented in this first edition of the Handbook represents the efforts of specialists in the various areas of reactor science and technology, and summarizes the accomplishments of the Commission's nuclear reactor program to date. Future editions are planned as continuing advances in this field may require.

The Commission extends its appreciation to all participants in the Reactor Program for the time and effort expended in the completion of this Handbook.

Lewis L. Strauss
Chairman
United States Atomic Energy Commission

REVIEW BOARD PREFACE

The Review Board was appointed by the Director of the Reactor Development Division in December of 1951. The Board found itself in agreement with the objective of preparing a reactor handbook at an early date, although it was recognized that this placed the effort under a considerable handicap as did the necessity of combining the efforts of numerous author groups.

The Board instituted a mechanism for review of the material as prepared by the author groups. In the work of review the members of the Board called upon many individuals in the various Laboratories for critical comments. Without this assistance the review could not have been performed in the two or three weeks usually available, and the members of the Board express their indebtedness and thanks to these reviewers.

The general format of the Handbook received consideration and the result is recognized as a compromise of what is most desirable in a handbook and what is practical under the present circumstances.

The ultimate success of the Handbook will depend a great deal upon the refinements in subject matter and presentation which will come about in subsequent revisions. It is expected that such revisions will profit enormously from suggestions from the users of the Handbook.

To the Editorial Coordinator, John F. Hogerton, to Donald F. Mastick who represented the Technical Information Service, and to William W. Galbreath who served as secretary, the Board expresses its appreciation for a cordial working relationship. Above all, thanks are due to the various author groups who made the task of review easier by their patience in receiving criticism and suggestions.

THE REVIEW BOARD

Harvey Brooks	Stephen Lawroski
Paul F. Gast	Miles C. Leverett
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EDITORIAL PREFACE

The purpose of the Reactor Handbook is to provide a condensed source of reliable data and reference information for those working in the reactor field. Work on this first edition, jointly sponsored by the Division of Reactor Development and the Technical Information Service, started in January 1952, with a fifteen-month publishing target. The authors, most of whom had heavy project commitments, had one month in which to plan their work, and three months to a year in which to survey the field and prepare their compilation. Those preparing large sections were called upon to submit their material in parts and were allowed on the average of one month for reworking a given part after review. The Review Board had the difficult task of reviewing the Handbook material in random increments, with two to three weeks in which to review a given increment. The schedule did not permit a second review following the author's reworking. The editors had from one to three weeks in which to prepare Handbook material for the publisher. To distribute the publisher's load at Oak Ridge, parts of sections were put into the publishing machinery while other parts were still in preparation by the authors.

To meet the schedule, it was necessary to make certain compromises which should be noted here:

1. A somewhat arbitrary approach has necessarily been taken on the problem of coverage, not only with respect to the subjects treated but also the data presented on a given subject. Before using a particular section for the first time, the reader should consult the author's preface which brings out any major limitations in the scope or treatment of the data presented.

2. The policy was adopted early in the program not to attempt a detailed documentation of the source of the data presented. Some specific references are given; however, source identification is restricted primarily to tables or figures which have been taken intact from project reports or the open literature.

3. It has not been possible to achieve the consistency one would like in the use of units. In general, the metric system is used where the data are considered to be of interest primarily to "scientists," and the English system is used where the data are considered to be of interest primarily to "engineers." An attempt has been made to include conversion factors in the body of tables and charts, and in some cases data are expressed in dual units.

4. To simplify page make-up and printing problems, the decision was made early in the program to eliminate the background grid from graphs. Data were to have been presented in tabular form in cases where it was considered important to retain accurate values. In actual practice some graphs have been reproduced with grid and it is felt that this practice can and should be extended in the next edition of the Handbook.

In the present edition of the Handbook, each volume is indexed separately. The organization is the same throughout. Sections are numbered consecutively within a volume; chapters consecutively within a section; and figures, tables, and formulae consecutively within a chapter.

EDITORIAL PREFACE

The first edition combines elements of a "Handbook of Chemistry and Physics," a Marks' "Mechanical Engineer's Handbook," a Mellor's "Treatise on Inorganic Chemistry," and an industrial data book. This result is in some degree inherent in a work that cuts across a number of scientific and engineering disciplines; however, greater unity of presentation should be possible in future editions.

The editors are most appreciative of the attention their problems have received from the Review Board and the author groups, and from Alberto F. Thompson and Donald F. Mastick of the AEC staff. They are most appreciative, also, of the cooperation of William W. Galbreath of ANL, W. H. Sullivan of ORNL and Dennis Puleston of BNL, who did much to advance the Handbook effort at their respective sites, and of R. L. Cummins, E. C. Schulte, and their publishing personnel in the Technical Information Service at Oak Ridge.

John F. Hogerton and Robert C. Grass
VITRO CORPORATION OF AMERICA

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Section 1

GENERAL PROPERTIES

Prepared by
BATTELLE MEMORIAL INSTITUTE
under the direction of
C. R. TIPTON, JR.

NOTE ON PREPARATION OF THE DECLASSIFIED EDITION

This declassified edition of the Reactor Handbook has been issued not only as a convenience to workers in the reactor field but also to help acquaint science and industry generally with techniques, processes, and equipment which may find wider application.

In preparing the volumes of the declassified edition, deletions were made in the classified volumes according to security requirements—the remaining material was then assembled with the minimum editorial attention necessary for coherent presentation. Since this procedure has not, in general, provided for bringing the data up to date, users of these declassified volumes should consult section prefaces to determine how old the data is in each section.

AUTHOR'S PREFACE

The development of materials for the construction of reactors has been in progress at an ever-increasing rate for more than ten years. This effort has produced a mass of information in scattered reports. With few exceptions, notably the Project Handbook of 1945, there have been only limited and sporadic attempts to compile useful engineering summaries. For the most part, workers in the field of materials have been too busy to undertake the compilation of handbooks. They have always found themselves pressed by the designers, struggling to solve the problem of the moment, with little time for the collection, let alone the compilation, of handbook data. There was also the question of what to put in a handbook on reactor materials. For a long time, much of the available information applied to specific reactors and was of limited value in a handbook for a designer thinking up new reactors.

The appearance of this volume does not mean that all of these difficulties have been resolved. But the metallurgists are still busy, and there are still gaps in the knowledge of such old materials as uranium and graphite, not to mention the new materials that will be used in reactors of the future. Perhaps the principal reason for the appearance of the present volume is that even the expert had begun to feel the need of a compilation in his own field of specialization. He could no longer remember all of the pertinent facts needed in his day-to-day work. Nor could he readily find the information in the collection of reports. This situation is the earmark of a mature technology, one that needs handbook coverage.

In preparing this section on the properties of materials, the Battelle Author Group had as an important objective, the summarizing of material useful for metallurgists, ceramists, and other workers in the field of materials. Attention was also given to making the data useful to workers in other fields of reactor technology. The problem of what to include and what to leave out has been a major one. With such subjects as uranium or zirconium metallurgy, where the information is largely in classified sources, the coverage has been reasonably complete. Chapters dealing with subjects like stainless steels, on the other hand, where there is a tremendous volume of information in the open literature, were limited to general highlights and selected topics judged to be of particular value in reactor design.

The materials treated are those which have been used or considered for use in reactors. No attempt has been made to define the materials of the future. Only solid materials are included. Liquid metals, as an example, are the subject of a section of the Engineering volume.

The treatment of the various materials has been generally formalized around the sequence of processing operations. Hence, extraction and recovery precede the discussions of melting and casting and metallography. Tables and figures have been used where possible, an objective being a large ratio of tables and figures to text. In textual matter, an attempt has been made toward conciseness.

The metric system has been used for all scientific data, i.e., chemical and physical constants, since most of these are determined in the cgs system. All other data, being

AUTHOR'S PREFACE

engineering in character, have been given in the English system. In a few selected cases, i.e., density, specific heat, and thermal conductivity, where both systems of units are common, a conversion from the cgs to the English system is given.

The extent of the documentation of data was decided as a policy for the Handbook, rather than for this section alone. In compliance with this decision, there is practically no documentation. Authors have had the responsibility of selecting "best" values from all available sources. Credit has been given for tables or figures taken from a single source.

A chapter author (generally a Battelle staff member) has prepared the subject matter on each of the materials covered. In many cases, he was assisted by various people throughout the project. In all cases, however, the authors are responsible for the accuracy and content of their chapter.

To name all those persons who contributed to this section would be impossible. The authors are indebted to all personnel of the project, since we have used liberally of everyone's efforts. Particular thanks, however, is due H. W. Russell and H. R. Nelson of Battelle Institute for their unfailing cooperation, guidance, and editorial assistance without which this section would never have been completed. Grateful acknowledgment is made to F. G. Foote, ANL, H. H. Hausner, SEP, and A. R. Kaufmann, MIT, for their review and comments on "Uranium and Its Alloys" and "Zirconium and Its Alloys"; to D. H. Gurinsky, BNL, J. J. Katz, ANL, D. W. Lillie, AEC, J. M. Taub, LASL, and R. Ward, HEW, for their review and comments on "Uranium and Its Alloys"; to R. C. Dalzell, AEC, W. A. Johnson, WAPD, Capt. H. G. Rickover, USN, and S. M. Shelton, BM, for their review and comments on "Zirconium and Its Alloys"; to J. H. Frye, ORNL, and B. A. Rogers, Ames Laboratory, for their review and comments on "Thorium and Its Alloys"; to A. U. Seybolt, KAPL, for his contribution to "Vanadium and Its Alloys" and his review and comments on "Uranium and Its Alloys"; to E. N. Skinner, International Nickel Company, for his review and comments on "Nickel and Its Alloys"; to F. H. Spedding, Ames Laboratory, for his review and comments on "The Rare Earths"; to Fred White, AEC, for his review and comments on "Graphite"; and to H. A. Wilhelm, Ames Laboratory, for his review and comments on "Thorium and Its Alloys" and "Uranium and Its Alloys."

November 11, 1952

C. R. Tipton, Jr.

Note to the Declassified Volume

This declassified section of the Reactor Handbook represents the realization of a readily-available volume of information for the general public. However, there are limitations and reservations which must be realized in utilizing the information in its present form.

While the organization and philosophy of this declassified volume represents no major change from that of the original, it must be remembered that the original version was intended for Project use. As a result, it contained material which has been deleted to make this volume declassifiable. No over-all attempt has been made to revise or rewrite the remaining material. Rather, after the required deletions were made, the remaining data were assembled editorially to make the smoothest possible presentation.

This declassified volume represents data up to about August, 1952. Having this volume, one has only to survey the literature from August, 1952, in order to bring himself up to date.

AUTHOR'S PREFACE

Grateful acknowledgment is made to Dr. H. W. Russell, Battelle Memorial Institute; Dr. Alberto F. Thompson, Atomic Energy Commission, Technical Information Service; and to Messrs. Gregory Abdian, Technical Information Service, Oak Ridge Extension, and W. A. Strauser, Declassification Branch, Oak Ridge Extension, for their guidance, assistance, and encouragement in the preparation of this declassified volume.

January, 1955

C. R. Tipton, Jr.

CHAPTER 1.1

Functions of Reactor Materials

E. M. Simons

From the beginning of our atomic energy program, technologists have been faced with many new and trying materials problems. To the usual considerations of physical and chemical properties was added a completely new materials criterion, nuclear properties. Cost, which had always been a dominant factor, became of minor importance. Since the physical, chemical, and nuclear properties required for reactor use have been found only in unusual materials, or in some exceedingly pure common materials, workers had to devise methods for producing commercial quantities of exceptionally pure elements and compounds from materials, many of which previously had been laboratory curiosities.

It is clear that the problems faced were staggering. For example, up to 1940, the total amount of uranium metal produced in this country was not more than a few grams, and even this was of doubtful purity. At the same time, the nation's gross output of metallic beryllium or zirconium could be held in the palm of a man's hand. Deuterium had been discovered only eight years before; heavy water was imported by the liter from Norway; and carbon had never been produced in quantity with anywhere near the purity required of a satisfactory moderator. There were huge voids in the knowledge of nuclear constants, and no one was able to predict with confidence how various materials would behave under pile radiations.

Since 1940, remarkable strides have been made in the development of materials for atomic weapons and low-temperature research reactors. However, the fact remains that ordinary engineering materials generally are not suitable for reactor use, particularly in the case of high-temperature power and breeder reactors. The best high-temperature alloys contain cobalt for which the neutron-capture cross section is much too high to permit their extensive use in thermal reactors. Refractory oxides, carbides, and nitrides suffer from generally poor resistance to thermal shock. The common low-cross-section metals, aluminum and magnesium, definitely are not high-temperature materials. Zirconium and beryllium have been produced only recently in pure form in commercial quantities, and even these metals cannot be used at very high temperatures. Thus, the reactor materials selection problem has resolved itself into a continuous struggle to overcome the drawbacks of common materials and to uncover new and more suitable ones.

Each component of a nuclear reactor poses its own special materials problems, although all must meet such basic requirements as adequate strength, corrosion resistance, and dimensional stability.

FUEL ELEMENTS

Heterogeneous reactor fuel elements usually are made up of a core, consisting of fissionable material dispersed in some diluent, and a cladding to contain the core and protect it from

corrosion, and to protect the coolant from fission-product contamination. In converters or breeders, the fertile material (either U^{238} or Th^{232}) also may be mixed or associated directly with the fuel.

Like all other components of a reactor core, fuel-element assemblies are called upon to meet rigorous demands.

1. They must have adequate strength under the most adverse conditions of temperature, irradiation, external loading, and weakening caused by burnup.
2. They must resist corrosion by neighboring materials and atmospheres.
3. They must be stable, both dimensionally and with respect to mechanical properties, under the operating conditions.
4. They must possess good heat-transfer properties, such as high thermal conductivity, large surface area, thin sections, and no dead spots.
5. They must have good nuclear characteristics, such as low-parasitic-capture cross section and low poison-forming tendencies.
6. They must be amenable to ready fabrication, installation, removal, and reprocessing.
7. In addition to the above requirements, canning materials should have good bonding characteristics and should not react chemically with the core. Also, there should be only minimum diffusion between core and cladding.

The selection of specific materials for fuel elements depends on such over-all considerations as whether the reactor is to produce power alone or breed; whether it is to be thermal, intermediate, or fast; availability of material, temperature of operation, corrosiveness of the coolant; and a host of others.

Representative fuel-element materials for various reactors are given in Table 1.1.1. These may be divided roughly into three types: slugs, clad plates, and liquids or loose powders. Existing reactors using natural or slightly enriched uranium generally employ slug-type fuel elements. Most of the more recent solid-fuel reactor designs replace the canned uranium slugs by clad plates having a uranium alloy core and a bonded coating of some suitable alloy, such as aluminum-tin, zirconium-tin, or stainless steel. Aluminum alloy-clad fuel elements can be used only for low-temperature applications (up to about 400°F with water) because of their poor high-temperature strength and corrosion resistance. Zirconium and its alloys are somewhat better, although their upper limit is probably under 1000°F. Certain of the stainless steels have very good strength and corrosion resistance, and molybdenum is promising for up to possibly 2500°F. However, both iron-base alloys and molybdenum have the disadvantage of high thermal-neutron absorption cross section and would require enriched fuel.

Although this discussion deals mainly with solid materials, it is worthy of mention here that fluid fuels have strong advantages in that there can be no damaging thermal stresses in the fuel and that there are no complex fuel-element fabrication problems. Furthermore, with circulating liquid fuels, reprocessing and poison removal can be done on a relatively simple, continuous basis. Their disadvantages lie in the difficulty of finding suitable fuel-bearing liquids with low melting points and reasonably low vapor pressures at elevated temperatures and of obtaining corrosion-resistant container materials.

STRUCTURAL MATERIALS

The core of a nuclear reactor, while simple in principle, is actually a complex unit containing many structural components, such as supports or containers for fuel and moderator; ductwork, piping, valves, and fittings; control-rod sleeves and mechanisms; and shells, baffle plates, header chambers, and closures. The general requirements of structural ma-

Table 1.1.1—Fuel Elements and Cladding for Specific Reactors

Reactor	Purpose	Type	Fuel	Fuel elements	Cladding	Coolant
			Operating, Past or Present			
ANL, CP-2	Research	Thermal	Natural uranium & uranium oxide	Lumps of fuel imbedded in graphite	None	None
ORNL, X-10	Research and production of radioisotopes	Thermal	Natural uranium	Slugs, 1.1 in. diam \times 4 in. long	Aluminum can	Air
Hanford H	Converting, production of plutonium	Thermal	Natural uranium	Slugs	Aluminum canned fuel slugs	Water
ORNL, HRE	Experimental	Thermal	Enriched uranium	Water solution of UO_2SO_4 , 30–40 gm/liter	Stainless steel spherical vessel, 18 in. diam	Circulating fuel
Arco, EBR	Experimental, breeding and power production	Fast	Enriched uranium	Rods	Stainless steel	Sodium-potassium
Arco, MTR	Materials testing and reactor component design	Thermal	Enriched uranium	Uranium plates	Aluminum	Water
Los Alamos Research	Research	Fast	Plutonium	Rods	Mild steel	Mercury
Chalk River, NRX	Research, production of radioisotopes	Thermal	Natural uranium	Rods	Aluminum	Water
In Advanced Design or Construction						
STR (Mark I)	Power	Thermal	Enriched uranium		Zirconium, crystal bar	High-pressure water
STR (Mark II)	Power	Thermal	Enriched uranium		Sponge zirconium	High-pressure water
SIR	Power	Intermediate	Enriched uranium			Sodium
ANL, CP-5	Research	Thermal	Enriched uranium	Uranium Plates	Aluminum	Heavy water
CP-6	Plutonium production	Thermal	Natural uranium		Aluminum	Heavy water

materials are adequate strength, fabricability, thermal stability, radiation stability, satisfactory corrosion resistance, and desirable nuclear properties.

The number of elements suitable for structural use in thermal reactors is severely limited, since the only structural metals having cross sections lower than 0.5 barn/atom for thermal-neutron capture are zirconium, beryllium, aluminum, and magnesium. Until quite recently, zirconium was an "exotic" metal which had very little commercial application. AEC-sponsored research during the past several years has vastly increased the knowledge about the production, fabrication, metallurgy, and properties of zirconium. Improved purification techniques, notably hafnium removal, have resulted in a product with a lower capture cross section than was originally measured. This, coupled with a high melting point, excellent fabricability, and generally good corrosion resistance, makes zirconium a promising structural material for the core of a thermal reactor. However, the pure metal is difficult to produce and creeps more than is desirable. Its corrosion resistance to high-temperature water and its high-temperature strength are improved considerably by additions of a few percent of tin.

Beryllium is another metal which is promising for structural use, since it has a good moderating ratio as well as a high melting point. However, the supply is limited, it is highly toxic, it is difficult to fabricate, and its corrosion resistance is generally inferior to that of zirconium. Attempts to clad beryllium have met with no success.

The remaining two low-cross-section metals, magnesium and aluminum, are certainly not high-temperature materials. Aluminum technology is well established, and, indeed, aluminum has been used extensively as a structural material in low-temperature research and production reactors. Although the corrosion resistance of magnesium is generally poor, it has not been accorded the attention it merits, considering its low cross section and relative abundance. Alloying aluminum or magnesium with small amounts of other materials often can bring about significant improvements in mechanical properties.

A great many more structural metals become available if a higher cross section can be tolerated. These could be used in small quantities in a thermal reactor and extensively in an intermediate or fast reactor. Pure metals with moderate-capture cross sections and high melting points include niobium, iron, molybdenum, chromium, copper, nickel, vanadium, and titanium. Niobium has good mechanical properties but is in short supply. Chromium has not yet been developed in form suitable for structural use. The properties of iron and copper can be greatly improved by suitable alloy additions, so their use as pure metals is unlikely. Ductile vanadium, now available commercially, is a promising structural material both from strength and corrosion considerations. Because of its known refractory properties and unusually high thermal conductivity molybdenum is a likely possibility for high-temperature, structural applications. Titanium and titanium alloys have very high strength-to-weight ratios, good corrosion resistance in general, and many desirable physical properties. Titanium technology has advanced tremendously in recent years making titanium and its alloys likely prospects for structural use in intermediate reactors.

A large number of promising alloys can be produced from the pure metals of interest. Among the iron-base alloys, there are a host of stainless steels combining good corrosion resistance with good mechanical properties up to moderately high temperatures. Nickel and its alloys, such as Nichrome, Inconel, Hastelloy, Monel, Inconel "X," and many others, are also interesting as likely structural materials.

Although generally weak in tension and thermal-shock resistance, ceramics are the only good prospects as structural elements for very high temperature applications. Oxides such as beryllia, magnesia, silica, alumina, and zirconia are well known and widely used as refractory materials. Of the carbides, beryllium carbide, silicon carbide, and zirconium carbide are also likely prospects. In addition, there is an endless number of combinations of various oxides and carbides which can be formed to give improved properties; also, the vast new field of metal-ceramics gives promise of providing high-temperature structural materials having good strength and thermal conductivity.

CONTROL MATERIALS

The operating level in a reactor can be controlled by altering the neutron leakage, the amount of fuel present, or the neutron losses by parasitic capture. Leakage control may be effected by changing the reflector, the surface-to-volume ratio, or the amount of moderator. Fuel control involves adding or removing fuel in suitable increments for proper regulation. However, thermal piles and low-energy intermediate piles generally are controlled most easily by changing the amount of absorber present.

Absorbing controls, which may be introduced into the pile in a number of ways, should have the following properties:

1. A high cross section for the absorption of neutrons.
2. Adequate strength (for solid rods).
3. Low mass, to permit rapid movement with slight inertia effects.
4. Good resistance to corrosion by the coolant.
5. Stability, both chemical and dimensional, under heat and radiation.
6. Reasonable cost (good availability and fabricability).
7. Good heat-transfer properties for adequate cooling.

Of the natural elements having high absorption cross sections for thermal neutrons, boron and cadmium have been used most commonly because they more or less meet all of the requirements outlined and their metallurgy is well established. Quite recently, hafnium, removed as an impurity from zirconium metal, has become available in significant quantities, and the STR project is fabricating experimental hafnium control rods.

Gold, rhodium, and iridium, while moderately attractive from cross-section considerations, are not particularly suited as principal constituents of control rods because their structural properties are poor and their mass densities are rather high for rapid movement with low inertia. Furthermore, they all form highly radioactive isotopes upon absorbing neutrons.

The low melting points and structural weaknesses of indium and mercury preclude their use as solid control materials. Mercury might be used as a liquid poison, but its high vapor pressure and reactivity with most metals make it less attractive for higher temperature piles.

The remaining elements of high absorption cross section are rare earths which currently are not available in commercial quantities. However, intensive AEC-sponsored research since World War II has produced great advances in knowledge about rare earths, and it is conceivable that some of these materials would be on the market at a reasonable cost if the demand existed. The capture cross sections of some of the heavier rare earths do not fall off so rapidly with increasing neutron energy as they do for most materials. This characteristic suggests that certain rare earths might be well suited for use as absorbing controls in epithermal or intermediate piles.

There are a number of elements which have isotopes with unusually high cross sections. Examples of these are B^{10} , Cd^{113} , Sm^{149} , Gd^{157} , Yb^{169} , and Hg^{196} . Such isotopes might be used advantageously for control purposes if they were easily obtainable, perhaps as a by-product from some other separation program or from a pile as fission fragments. However, a high volume density of absorbing atoms is desirable, as well as high cross section, in order to ensure long life of the control rod. Another consideration here is the nature of the product resulting from neutron capture. Cd^{113} , for example, transforms by an (n, γ) process to stable Cd^{114} , so that the strength and corrosion resistance of a cadmium control rod would be virtually unaffected by high burnup. On the other hand, B^{10} transmutes to stable Li^7 by an (n, α) reaction with resulting undesirable changes in properties as the B^{10} atoms are used up.

The poison in a control rod generally is diluted with other elements to add structural strength and corrosion resistance. Such diluents either should be fair absorbers themselves or should be present in as small a concentration as possible in order to provide a maximum density of absorbing atoms. This permits greater burnup and longer control-rod life before replacement.

MODERATOR AND REFLECTOR MATERIALS

Moderating materials for thermal reactors should be capable of reducing neutron energy rapidly; this requires a low atomic weight. They must have a high-scattering cross section, a large, average logarithmic neutron-energy loss per collision, and a low absorption cross section for thermal neutrons.

From consideration of slowing down power and moderating ratio, it is apparent that good moderators will be composed of such elements as deuterium, oxygen, carbon, beryllium, and hydrogen. These elements may be compounded with others, provided the diluent materials have low capture cross sections and allow a large atomic density of the good moderators. Gases are too low in atomic density to be good moderators. Water, heavy water, hydrides, hydrocarbons, deuterocarbons, and other organic compounds are possible moderators, although the feasibility of the organic compounds is uncertain in view of their radiation sensitivity.

Beryllium and carbon or their compounds are the only good, solid moderators. Although beryllium is expensive and not very abundant in its pure metallic state, its very low capture cross section and high moderating ratio have led to its use in a number of reactors. Its compounds, beryllium carbide and beryllium oxide, are refractory materials which make good moderators for power-producing piles that must operate at elevated temperatures.

Carbon in the form of graphite was the first reactor moderating material ever used and is the moderator employed in many of the existing reactors. This is because it is relatively inexpensive, even in its pure state, abundant, easy to work, and has good physical properties. Also, it is a refractory material and can be utilized in high-temperature reactors in a nonoxidizing atmosphere.

Since the function of a reflector is to scatter or reflect as many leakage neutrons as possible back into the pile, the reflector must meet the same nuclear requirements as the moderator, viz., good scattering characteristics and a low probability of neutron capture. Hence, the same materials that are suitable as moderators are suitable as moderating reflectors. However, the primary function of a reflector is scattering, and many additional materials which are not considered good thermal-pile moderators but which have high-macroscopic-scattering cross sections for fast neutrons (0.1 to 4 Mev) are usable as fast reflector materials. Actually, there is some advantage in using reflector materials with high inelastic scattering and poor slowing-down characteristics, since parasitic-capture cross sections generally increase sharply with decreasing neutron energy. Suitable fast reflector elements include those with high atomic density (e.g., iron); those in the upper end of the periodic table for which atomic-scattering cross sections are high (bismuth, lead); and fertile breeder materials, which also have high-fast-scattering cross sections (uranium, thorium). Note that these elements have generally high densities, and their use as primary reflector constituents reduces the gamma-shielding requirements. However, the moderating ability of the shield would then have to be increased to compensate for fast neutron leakage from the nonmoderating reflector.

Thus far, only the nuclear requirements of moderator and reflector materials have been emphasized. In addition, solid moderators and reflectors must have all the attributes of a good structural material. These include adequate strength, fabricability, thermal stability,

radiation stability, and corrosion resistance. Furthermore, they must have good heat-transfer properties to dissipate the energy released by neutrons during attenuation.

SHIELDING MATERIALS

The basic requirements for a radiation shield around a nuclear reactor are (1) a good moderating material to slow down neutrons, (2) a good neutron absorber, and (3) a dense, heavy material for attenuating the gamma radiation. No one material answers all of these demands, except when it is used in large quantities. Therefore, radiation shields generally are composed of several materials, each having the ability to perform at least one of the above functions. A wide diversity of materials, divided roughly into the following classes, is of interest as shield constituents:

1. Amalgams
2. Cement and concretes of special aggregates
3. Ceramics and cermets
4. Glasses and fused salts
5. Metal ores
6. Metals, alloys, and sintered powders
7. Organics, such as plastics, elastomers, metal esters, metal-loaded resins, silicones
8. Silica and other gels precipitated from boron-loaded solutions
9. Water, hydrides, hydrates, and hydroxides

Boron is one of the most interesting of the light elements used for neutron shielding. Although its elastic-scattering cross section is low compared to hydrogen, it has an unusually high neutron-capture cross section in the lower energy regions.

Hydrogenous materials are excellent moderators and also have fairly good capture cross sections for thermal neutrons. However, the capture of neutrons by hydrogen is largely an (n, γ) reaction, producing secondary gammas which must in turn be attenuated by additional shielding. Ordinary water makes a satisfactory shield if enough thickness is used.

Nuclearwise, heavy metal hydrides appear to be ideal for shielding, since they could combine moderator, absorber, and gamma attenuator into a single compound, such as tungsten or tantalum borohydride. Not all metal hydrides are stable thermally, although such hydrides as titanium hydride, zirconium hydride, sodium hydride, potassium hydride, lithium hydride, and calcium hydride might be considered stable when they contain somewhat less than the stoichiometric amount of hydrogen. Other hydrides of possible interest for reactor shields include chromium hydride, tantalum hydride, boranes, aluminohydrides, and borohydrides.

The use of hydrates and hydroxides for shielding is subject to much the same restrictions as apply to hydrides. A hydrated hydroxide such as $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ might be suitable where the shield is not exposed to high temperatures. However, most compounds of this type lose water rapidly with increased temperature.

The organic hydrogenous compounds of potential shielding interest have three limitations: (1) low thermal stability, (2) susceptibility to oxidation at relatively low temperature, and (3) susceptibility to deterioration under radiation.

Concrete is a good structural material, can be handled easily, and contains enough hydrogen to moderate fast neutrons. Its density is low, and consequently an all-concrete shield will be thick. In the past few years, a great deal of development work has been done on special concretes for shields. Oxychloride cements have occupied considerable attention because of their high water content, high strength, and excellent workability. "MO" concrete is magnesium oxychloride cement with steel punchings and shot for aggregate. Other metallic oxyhalides were studied at some length, and a great many metals and cations are available as such cements. By-product rare-earth carbonates, with thermal-

neutron-capture cross sections exceeding that of pure boron, have been calcined, mixed with MgCl_2 solutions, and made into similar cements. The X-10 pile at Oak Ridge has a concrete shield made of Portland cement and haydenite (a porous, calcined water-absorbent shale), coated with a bituminous paint to retard water loss. This shield has shown remarkable water retention, freedom from radiation damage, and continued strength after more than five years of operation.

Lead, tungsten, and tantalum are the heavy metals of practical interest for shields, Gold, iridium, osmium, uranium, and the rare earths might be used, but initial cost and availability are limitations. Lead and tantalum are readily fabricable, and tungsten can be made into a wide variety of shapes by powder-metallurgy methods. All three metals oxidize readily in air at elevated temperatures and would have to be coated if such service is required.

CHAPTER 1.2

Aluminum and Its Alloys

N. F. Ritchey* and C. M. Craighead

In this chapter, data are presented only for those alloys which appear most promising from reactor considerations. For instance, casting alloys were chosen assuming that low thermal cross section and corrosion resistance were the most desirable properties, although it is recognized that certain reactor designs may require better alloy performance at moderately elevated temperatures at some expense to neutron economy. Consequently, some copper-bearing alloys which have higher strength at and above room temperature are included.

Wrought alloys were selected so that product coverage could be realized with reasonable regard for nuclear considerations. The alloys, which are generally available in a variety of forms, are discussed: Comparatively pure alloys, 2S and 3S; high-strength copper-bearing alloys, 17S and 24S; medium-strength alloys, 61S and 63S, which possess good corrosion resistance and low thermal cross section; and 52S, a strain-hardenable alloy possessing a desirable combination of forming characteristics, low thermal cross section, and good corrosion resistance.

Tables 1.2.1 and 1.2.2 list the chemical composition of selected cast and wrought aluminum alloys, respectively.

REACTOR APPLICATION

Because of its low thermal-neutron-absorption cross section and corrosion resistance, aluminum warrants favorable consideration as a structural material and as a protective coating for fuel elements. However, its low melting point, decreased high-temperature strength, and lowered corrosion resistance of most of the higher strength alloys limit its use to low-temperature applications. At present, the principal applications are in the canning and cladding of fuel elements and as pilot tubes in water-cooled reactors.

ABUNDANCE AND AVAILABILITY

Aluminum is one of our more abundant metals, but in recent years production of the metal by the three U. S. producers, Alcoa, Reynolds, and Kaiser, has been insufficient to supply the demand adequately. This condition is being rectified rapidly.

In 1950, aluminum production amounted to 705,000 tons. The 1951 production of primary metal was 820,000 tons, and when all new facilities are in operation in 1953, production

* AEC Engineering Division, Reynolds Metals Company.

Table 1.2.1—Chemical Composition Limits of Selected Aluminum Casting Alloys

Alloy	ASTM designation	Cu		Fe		Si		Mn		Mg		Zr		Cr		Ti		Ni		Sn		Others		Al
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Each max	Total max	
13*	S12A	...	0.6	0.8	11.0	13.0	0.3	...	0.1	0.3	0.05	0.1	0.2	Remainder	
43*,†,‡	S5A1	.8	4.5	6.0	.305	.2	0.05	.15	Remainder
122†,‡	CG100A	9.2	10.8	1.5	1.0	3.0	.5	0.15	.35	.5	0.3	0.3	Remainder
A132†	SN122A	0.5	1.5	1.0	11.0	13.0	.1	.9	1.3	.1	2.0	3.0	0.05	...	Remainder
142†,‡	CN42A	3.5	4.5	0.8	...	0.6	.1	1.2	1.8	.1	0.2	.2	1.7	2.305	0.15	Remainder
214†	G4A	...	0.1	.43	.3	3.5	4.5	.105	.15	Remainder
218*	G8A2	.83	.3	7.5	8.5	.1	0.1	0.12	...	Remainder
220†	G10A2	.32	.1	9.5	10.6	.1	0.05	.15	Remainder
356†,‡	SG70A2	.5	6.5	7.5	.1	0.2	.4	.205	.15	Remainder
360*	SG100A6	.8	9.0	10.0	.3	.4	.6	.5	0.5	0.12	...	Remainder

* Die-casting alloy

† Sand-casting alloy

‡ Permanent-mold alloy

Table 1.2.2—Chemical Composition Limits of Selected Wrought Aluminum Alloys

Alloy	Si	Fe		Cu		Mn		Mg		Cr		Zn		Ti		Others		Al
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Each max	Total max	
2S	...	*	*	...	0.20	...	0.05	0.10	0.05	0.15	99.0
3S	...	0.60	0.7020	1.0	1.51005	.15	Remainder
17S80	1.0	3.5	4.5	0.40	1.0	0.20	0.80	...	0.10	.1005	.15	Remainder
24S50	0.50	3.8	4.9	.30	0.90	1.2	1.810	.1005	.15	Remainder
52S	...	†	†	...	0.1010	2.2	2.8	0.15	.35	.1005	.15	Remainder
61S	0.40	0.80	0.70	0.15	.4015	0.80	1.2	.15	.35	.20	0.1505	.15	Remainder
63S	.20	.60	.351010	.45	0.8510	.10	.1005	.15	Remainder

* 1.0 Si + Fe

† 0.45 Si + Fe

will reach an all-time U. S. high of about 1,300,000 tons. The Aluminum Company of Canada is also expanding its production capacity with the construction of a new plant at Kitmat, B. C. By 1954, Canada will be producing an additional 100,000 tons of aluminum per year. With these increased facilities, aluminum, based on present day consumption, should not be in short supply in the foreseeable future.

COST

In July 1952, unofficial reports indicated that prices will rise on aluminum. The June 1952 price range is given below:

Product	Approximate price range*
Wire, rod, and bar	37–45 cents/lb
Extrusions and tubing	50–60 cents/lb
Sheet products	30–35 cents/lb
Virgin pig	18 cents/lb
Virgin ingot	19 cents/lb
Alloy ingot	21–22 cents/lb

* Specific price depends upon alloy, temper, size, finish, etc.

EXTRACTION AND PURIFICATION

While aluminum silicate minerals are among the chief components of the earth's crust, they are not utilized to any extent in the production of aluminum. Bauxite is the recognized low-cost ore material. Commercial-grade bauxite, suitable for the Bayer extraction process, contains between 50 and 60 percent of Al_2O_3 and not more than 7 percent of SiO_2 .

The ore is an intimate mixture of hydrated aluminum oxides, chiefly Gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), with some kaolin or clay, and iron and titanium minerals, which are present in varying amounts. Bauxite deposits are residual ore bodies derived from the weathering of igneous and sedimentary rocks and occur as irregular pockets or layers, generally near the surface.

U. S. reserves of high-grade bauxite were severely depleted during the war years, but vast high-grade bauxite deposits, existing in South America and the Caribbean area, are adequate to supply our industry for many years to come. In case the importation of foreign bauxite were cut off, other processes are available to extract alumina from low-grade domestic ores at an increased cost.

Aluminum cannot be produced directly from the ore. Pure alumina is extracted chemically from bauxite by hot digestion under pressure with a strong solution of caustic soda. Under these conditions, the alumina content of the bauxite dissolves as sodium aluminate. After some dilution of the charge with water, the soluble sodium aluminate liquor is separated from the insoluble portion of the ore by filtration. This filtrate is then seeded with some previously precipitated aluminum trihydrate, and the liquor is agitated to precipitate the bulk of the aluminate as aluminum trihydrate. The precipitated hydrate is filtered, washed, and calcined to produce pure aluminum oxide. The depleted sodium aluminate liquor is concentrated and recycled for digestion of more bauxite.

A very-high-purity alumina is required for subsequent electrolysis of the oxide to metal, because any impurities, such as iron, silicon, or other heavy metals, are reduced in the electrolytic process. The following analysis of calcined alumina is typical of the purity of the material produced by the Bayer Process:

Component	%
Total water	0.18
SiO ₂	.05
Fe ₂ O ₃	.04
Na ₂ O	.18
Al ₂ O ₃	99.55

Silica is the only impurity ordinarily present in bauxite which must be controlled for the Bayer extraction. In normal operation for each percent (or pound) of silica in the ore, approximately 1.1 percent (or pounds) of alumina and 1.2 percent (or pounds) of soda ash are lost in the insoluble residue. Consequently, loss of alumina and soda is held to a minimum by specifying that the silica content of Bayer-grade bauxite shall not exceed 7 percent SiO₂.

During World War II, while shipping of high-grade bauxite from South America was hazardous, a combination process was used to treat the lower-grade domestic ores. This secondary treatment, known as the lime-soda-sinter process, or as the combination process when combined with the Bayer Process, utilizes the insoluble residue from the Bayer digestion to recover both alumina and soda that would otherwise be lost in the Bayer treatment of high-silica bauxite. The red mud from the Bayer digestion, containing the insoluble constituents of the ore, is sintered with high-calcium limestone and soda ash. This sinter is leached to recover alumina and soda, and the leach liquor is returned to the Bayer cycle.

The reduction of alumina to metallic aluminum is an electrolytic process carried out at about 1830°F in a fused cryolite bath in which the alumina is soluble. Carbon-lined steel pots and carbon electrodes extending into the molten cryolite form the electrolytic cell. Usually about 100 pots are connected in series and operate at about 7 volts. As electrolysis proceeds, additional alumina is added to the cryolite and the molten metal is tapped periodically as it accumulates in the pot. The purity of the metal averages better than 99 percent aluminum but seldom exceeds 99.7 percent.

Metal of 99.9+ purity is produced electrolytically in a cell of three liquid layers, the Hoope's refining cell, operation of which depends on the differences in density between pure molten aluminum, the electrolyte, and the anode metal. The anode metal is an aluminum-copper alloy containing 25 to 30 percent copper and preferably enough silicon to lower the freezing point considerably so that the alloy will remain molten even when the aluminum has been largely reduced by electrolysis. The molten anode metal, having a greater density than either the electrolyte or the refined aluminum, forms the bottom layer of the three-layer cell. The electrolyte, with an intermediate density, is composed of a mixture of cryolite, sodium fluoride, and barium fluoride nearly saturated with alumina.

Pure aluminum, with a density of about 2.3 at 1830°F, forms the top layer of the three-layer cell. As electrolysis proceeds, impure aluminum or aluminum-copper alloy is added, and refined cathode metal is tapped. As impurities build up in the anode, metal is periodically tapped off to maintain the proper metal level and freezing point.

PHYSICAL AND CHEMICAL CONSTANTS

Table 1.2.3 lists the principal physical and chemical constants for pure aluminum; Tables 1.2.4 and 1.2.5 list the more important engineering constants for the selected cast and wrought alloys, respectively.

Table 1.2.3—Physical and Chemical Constants of Aluminum

Thermal-neutron absorption cross section, barns/atom	0.215 ± 0.008
Density,* gm/cm ³	
Calculated	2.694
Measured	2.699
Melting point, °C	660.2
Boiling point, °C	2327
Vapor pressure, atm	
1017°C	10 ⁻⁴
1272°C	10 ⁻⁴
1667°C	10 ⁻²
Heat of fusion, cal/mole	2,550
Volume increase on fusion, %	6.6
Heat of vaporization, cal/mole	67,900
Specific heat,† cal/(gm)(°C)	
-150°C	0.1367
0°C	.2079
100°C	.225
300°C	.248
600°C	.277
Enthalpy or heat content, (H _T - H _{25°C}), cal/gm	
100°C	22.59
200°C	45.94
300°C	70.07
400°C	94.97
500°C	120.64
600°C	147.09
Coefficient of linear thermal expansion, per °C	
20°-100°C	23.8 × 10 ⁻⁶
20°-200°C	24.7 × 10 ⁻⁶
20°-400°C	26.7 × 10 ⁻⁶
20°-600°C	28.7 × 10 ⁻⁶
Electrical resistivity, μohm-cm	
-189°C	0.64
-100°C	1.53
0°C	2.63
20°C	2.66
100°C	3.86
400°C	8.0
Thermal conductivity,‡ cal/(sec)(cm)(°C)	
Room	0.503
100°C	.503
200°C	.530
400°C	.546
Crystallography	
Structure	Face-centered cubic
Lattice constant	a = 4.0489Å
Health hazards	None
Handling and storage	No problems

* Gm/cm³ × 62.43 = lb/cu ft

† Cal/(gm)(°C) × 1 = Btu/(lb)(°F)

‡ Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

Table 1.2.4—Physical and Chemical Constants for Selected Casting Alloys

Alloy	Density, gm/cm ³	Approx. melting range, °C	Electrical conductivity (20°C), % IACS*	Thermal conductivity (25°C), cal/(sec)(cm)(°C)	Coefficient of thermal expansion (20°–300°C), per °C
13†	2.69	570–585	39	0.37	21.6×10^{-6}
43	2.69	570–620	37	.35	23.9
43†	2.69	570–620	42	.39	...
122-T2	2.68	490–620	41	.38	...
122-T61	2.95	490–620	33	.31	...
122†	2.76	490–620	34	.32	23.4
142-T21	2.81	530–630	44	.40	...
142-T571†	2.81	530–630	34	.32	24.5
142-T77	2.81	530–630	38	.35	...
142-T61†	2.81	530–630	38	.31	24.5
214	2.65	580–640	35	.33	23.9
214†	2.65	580–640	35	.33	...
218†	2.60	530–615	24	.24	24.1
220-T4	2.57	450–620	21	.21	24.5
356-T51	2.68	570–615	43	.40	21.4
356-T6	2.68	570–615	39	.36	21.4
356-T7	2.68	570–615	40	.37	...
356-T6†	2.68	570–615	41	.36	...
360†	2.68	555–595	37	.35	...

* IACS—International Annealed Copper Standard

† Chill-cast samples; all others cast in green-sand molds

‡ Annealed; while castings are not commonly annealed, similar effects on conductivities may result from the slower rate of cooling of thick sections as compared with thin ones and other variables in foundry practices; comparison of the values for as-cast and annealed specimens will show the extent to which variations may be expected, depending upon the differences in the production of different types of castings

Table 1.2.5—Physical and Chemical Constants for Selected Wrought Aluminum Alloys

Alloy	Density, gm/cm ³	Approx. melting range, °C	Electrical conductivity (20°C), % IACS*	Thermal conductivity (25°C), cal/(sec)(cm)(°C)	Coefficient of thermal expansion (20°–300°C), per °C
EC-O	2.70	650–660	62	0.56	23.8×10^{-6} †
EC-H19	2.70	650–660	62	.56	23.8†
28-O	2.71	640–660	59	.53	25.6
28-H18	2.71	640–660	57	.52	25.6
38-O	2.73	640–655	50	.46	25.0
38-H12	2.73	640–655	42	.39	25.0
38-H14	2.73	640–655	41	.38	25.0
38-H18	2.73	640–655	40	.37	25.0
178-O	2.79	510–585	45	.41	25.0
178-T4	2.79	510–585	30	.29	25.0
248-O	2.77	500–635	50	.45	24.7
248-T3	2.77	500–635	30	.29	24.7
528-O	2.68	590–650	35	.33	25.7
528-H38	2.68	590–650	35	.33	25.7
618-O	2.70	580–650	45	.41	25.4
618-T4	2.70	580–650	40	.37	25.4
618-T6	2.70	580–650	40	.37	25.4
638-T42	2.70	615–650	50	.46	25.2
638-T5	2.70	615–650	55	.50	25.2
638-T6	2.70	615–650	55	.50	25.2

* IACS—International Annealed Copper Standard

† 20° to 100°C only

MECHANICAL PROPERTIES*

TENSILE

Figures 1.2.1 and 1.2.2 give the tensile and yield strengths of cast and wrought aluminum alloys at room temperature, 400°, and 600°F. Figure 1.2.3 shows the elongation and hardness of various cast and wrought alloys at room temperature.

SHEAR STRENGTH

Figure 1.2.4 shows the relative shear strength of various cast and wrought aluminum alloys at room temperature.

ELASTIC MODULUS

The elastic moduli at room temperature of selected alloys, as well as the variation of modulus with temperature, are given in Table 1.2.6.

CREEP DATA

Figure 1.2.5 shows the effect of temperature on stress to produce a minimum creep rate of 0.001 percent/hr for selected wrought aluminum alloys. One of the most complete references on creep characteristics of various aluminum alloys at moderate to elevated temperatures is Rand Project Report R-104.† For example, 16 minimum creep-rate curves and 85 design curves are available for specific design data.

Some casting alloys have lower creep rates than the wrought alloys, and this, according to the Rand report, may be attributed to differences in grain size or stabilization. The fundamental cause of the effects of various variables such as grain size is not too well understood at this time so that unavoidable discrepancies in experimental data are noted.

Design curves for 2S-O aluminum sheet at 400°, 450°, 500°, and 550°C are given in Figs. 1.2.6 to 1.2.9. Similarly, design curves for J51S sheet (0.7% Mg, 0.4% Si, 0.25% Cu, and balance aluminum) at 300°F (149°C) after a special heat treatment (5 min at 1100°F, furnace cooled to 975°F, air quenched and aged 3 hr at 325°F) are given in Figs. 1.2.10 and 1.2.11.

Design curves for extruded 63S in the T5 and T6 tempers at 90°, 212°, 300°, and 400°F are given in Figs. 1.2.12 and 1.2.13.

A recently developed wrought aluminum alloy (6% Mg, 0.5% Cr, 0.10% Ti, and balance aluminum) is of interest from the standpoint of creep and high-temperature properties, thermal-neutron cross-section value, and corrosion resistance in boiling distilled water. This alloy is reported (BMI-T-38) to have creep characteristics at 600°F of the same order of magnitude as 24S-T3, after stabilizing for 24 hr at 600°F; outstanding tensile properties at all temperatures up to 600°F; a thermal-neutron cross-section value similar to that of pure aluminum, and a corrosion resistance in boiling, distilled water at 212°F of the same order as 2S and 72S.

FATIGUE STRENGTH

Fatigue strength, like tensile strength, is decreased by higher temperatures. Stabilization periods also have a noticeable effect on fatigue and tensile properties, being considerably higher after short periods of stabilization than after prolonged heating.

* The mechanical properties discussed herein are typical rather than guaranteed minimum properties.

† C. M. Craighead, L. W. Eastwood, and C. H. Lorig, *An Appraisal of the Usefulness of Aluminum Alloys for Supersonic Aircraft and Guided Missile Construction*, August 8, 1940.

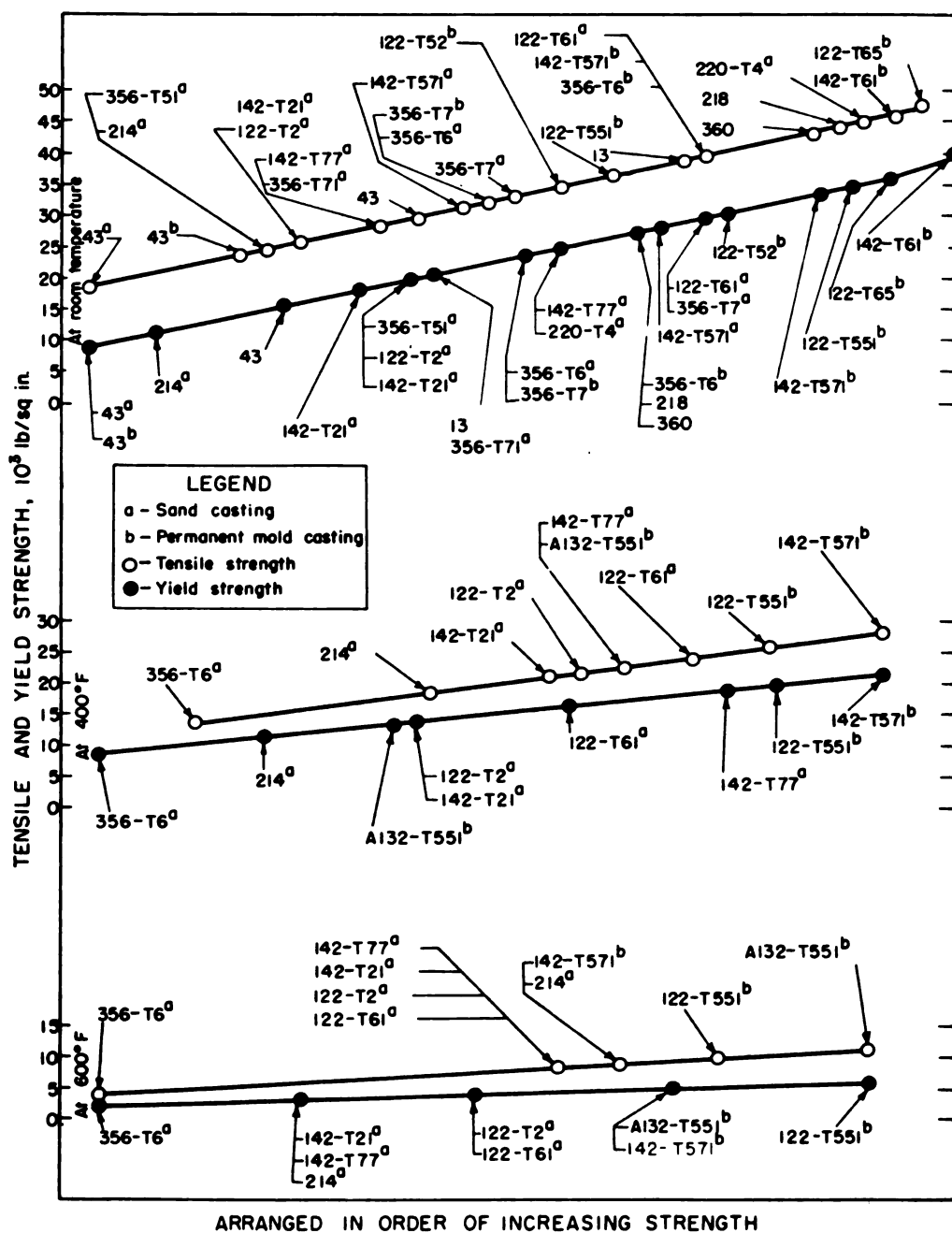


Fig. 1.2.1—Relative Tensile and Yield Strengths of Cast Aluminum Alloys at Room Temperature, 400°, and 600°F. Constructed from aluminum producers data by Battelle Memorial Institute, Aug. 1, 1952. For significance of temper designations refer to discussion of heat treatment.

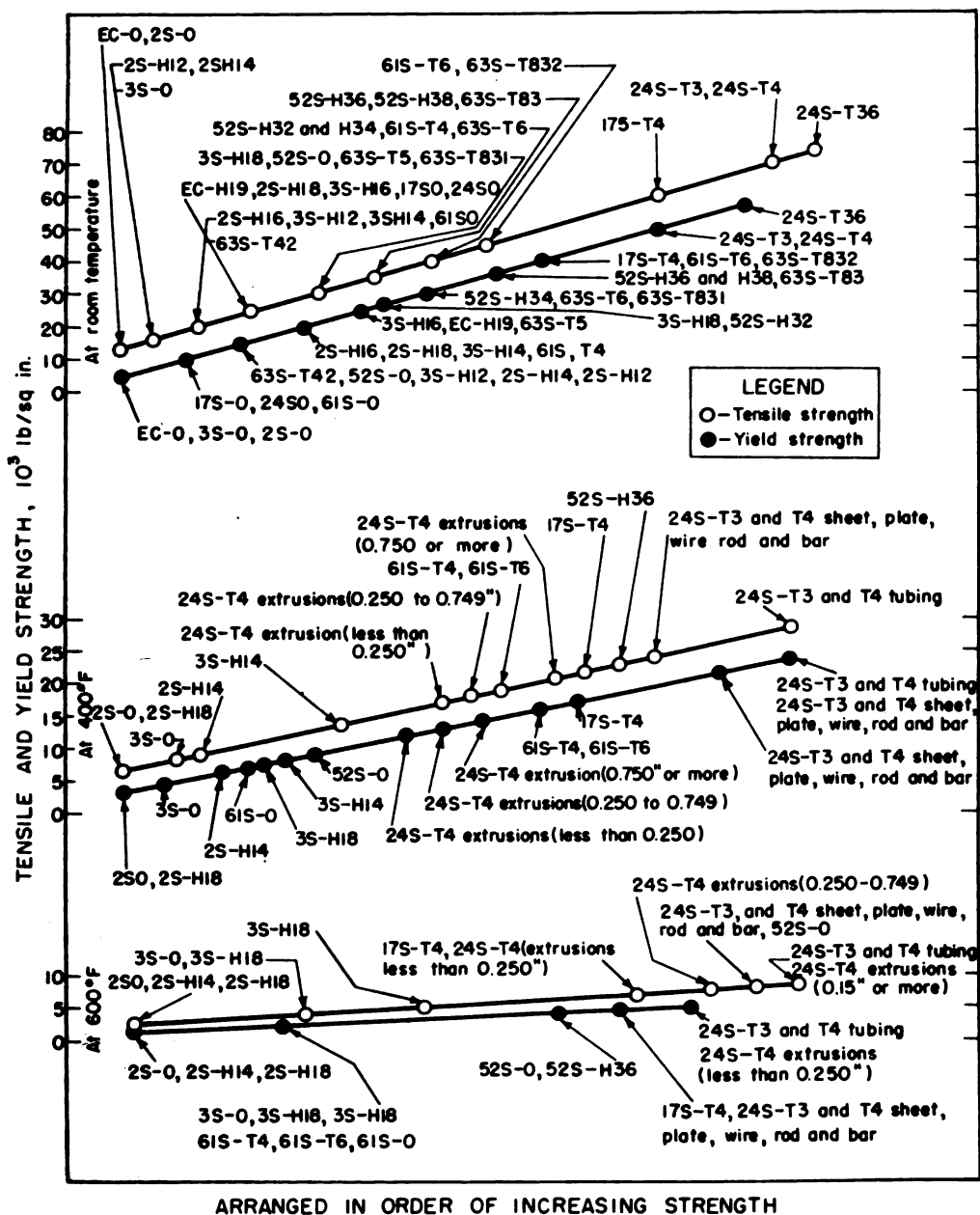


Fig. 1.2.2—Relative Tensile and Yield Strengths of Wrought Aluminum Alloys at Room Temperature, 400°F, and 600°F. Constructed from aluminum producers data by Battelle Memorial Institute, Aug. 1, 1952. Room-temperature properties based on typical properties. For 400° and 600°F, properties stabilized 10,000 hr (except 2S and 3S—5000 hr) at 400° or 600°F before testing. For significance of temper designations refer to discussion of heat treatment.

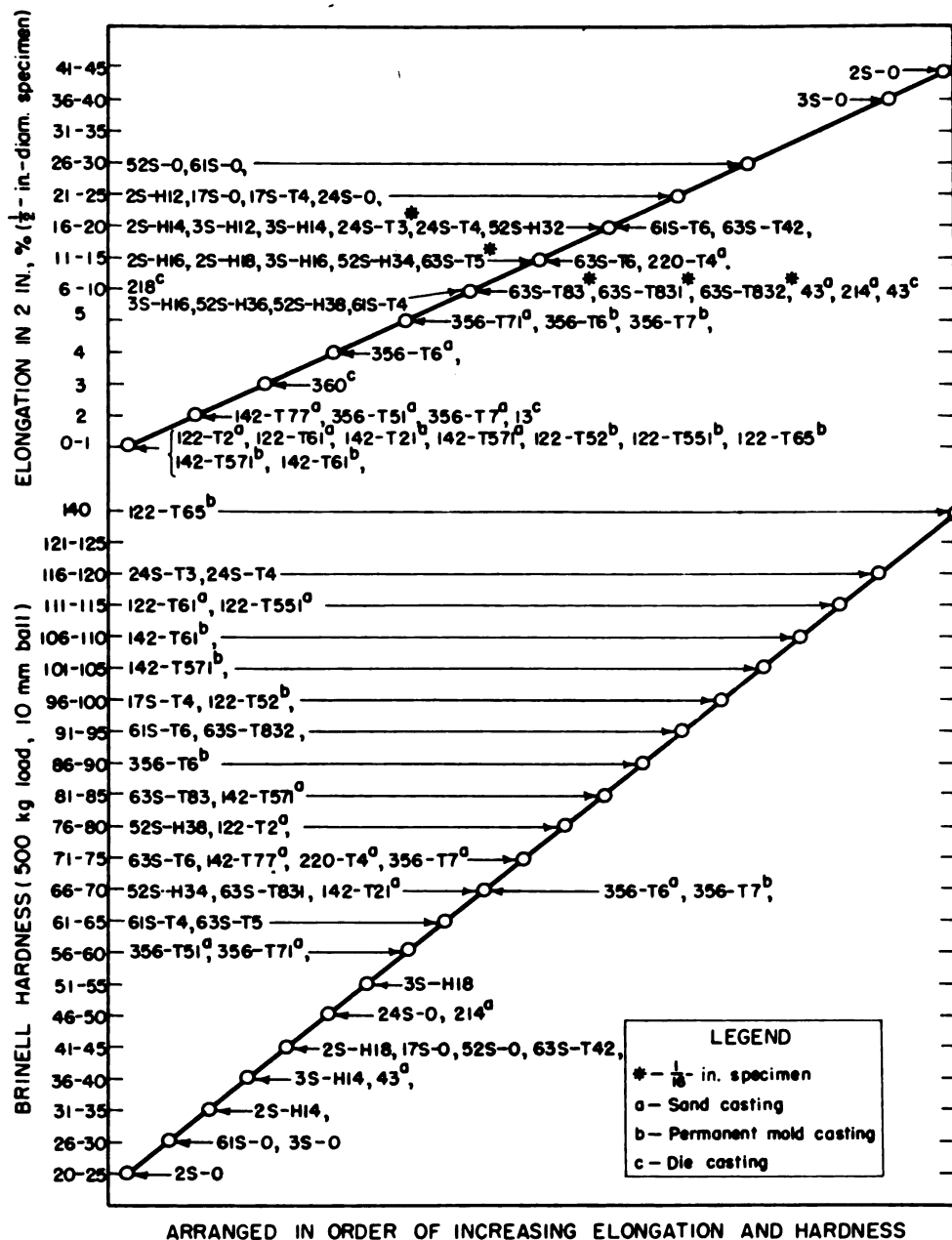


Fig. 1.2.3—Relative Percent Elongation and Brinell Hardness of Wrought and Casting Alloys at Room Temperature. Constructed from aluminum producers data by Battelle Memorial Institute, Aug. 1, 1952. For significance of temper designations refer to discussion of heat treatment.

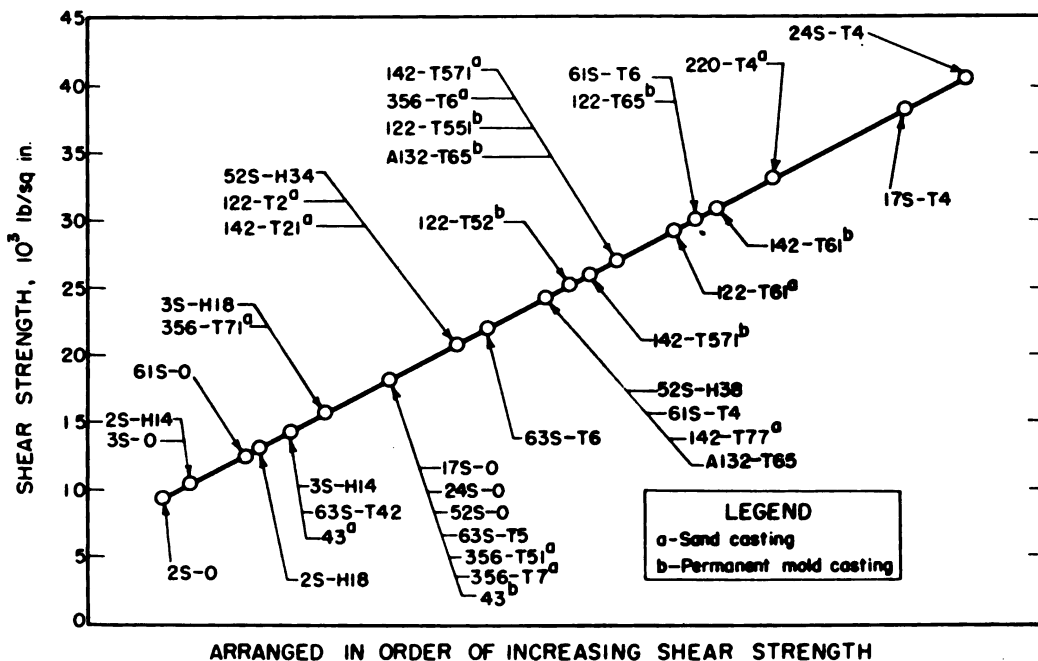


Fig. 1.2.4—Relative Shear Strength of Wrought and Casting Alloys Tested at Room Temperature. Constructed from aluminum producers data by Battelle Memorial Institute, Aug. 1, 1952. For significance of temper designations refer to discussion of heat treatment.

Table 1.2.6—Modulus of Elasticity of Aluminum Alloys in Tension

Alloy	Average modulus, lb/sq in.*		
	75°F	300°F	500°F
2S, 3S, 61S, and 63S	10,000,000	9,500,000	8,000,000
52S	10,200,000	9,700,000	8,150,000
17S	10,500,000	10,000,000	8,400,000
14S and 24S	10,600,000	10,100,000	8,500,000
Aluminum casting alloys	10,300,000	9,800,000	8,250,000

* The modulus of elasticity is about 2% higher in compression than in tension. For most calculations, a value of 10,300,000 lb/sq in. can be used for all alloys in both tension and compression. The modulus of rigidity is approximately 3,900,000 lb/sq in., and Poisson's ratio is about $\frac{1}{3}$

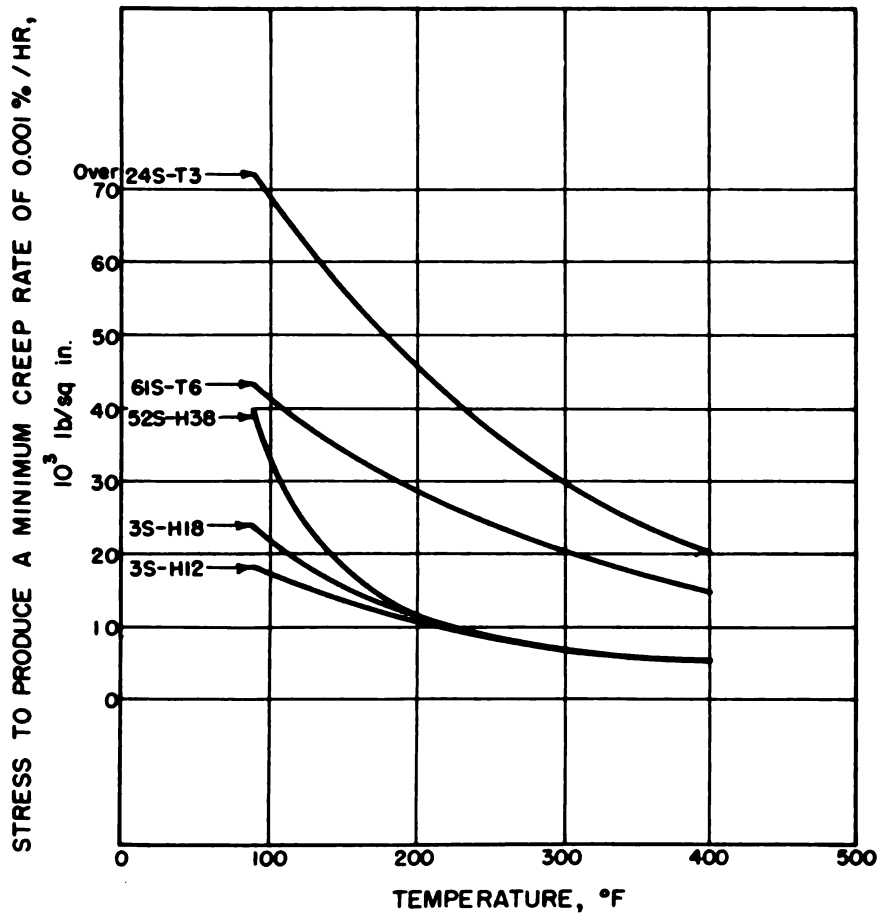


Fig. 1.2.5 — Effect of Temperature on Stress to Produce a Creep Rate of 0.001% hr for Several 0.065-in.-thick Wrought Alloys. Constructed from aluminum producers data by Battelle Memorial Institute, Aug. 1, 1952. For significance of temper designations refer to discussion of heat treatment.

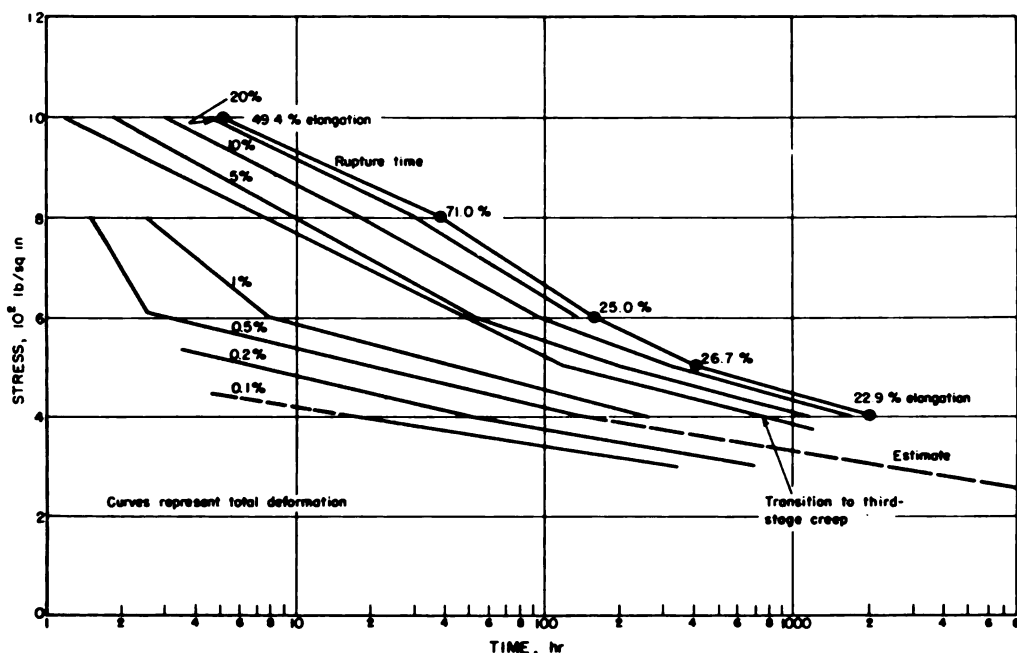


Fig. 1.2.6—Design Curves for 2S-O Aluminum Sheet at 400°C. Reprinted from W. F. Simmons and H. C. Cross, Creep of 2S-O Aluminum Sheet at 400° and 450°C, Battelle Memorial Institute, BMI-T-29, June 9, 1950.

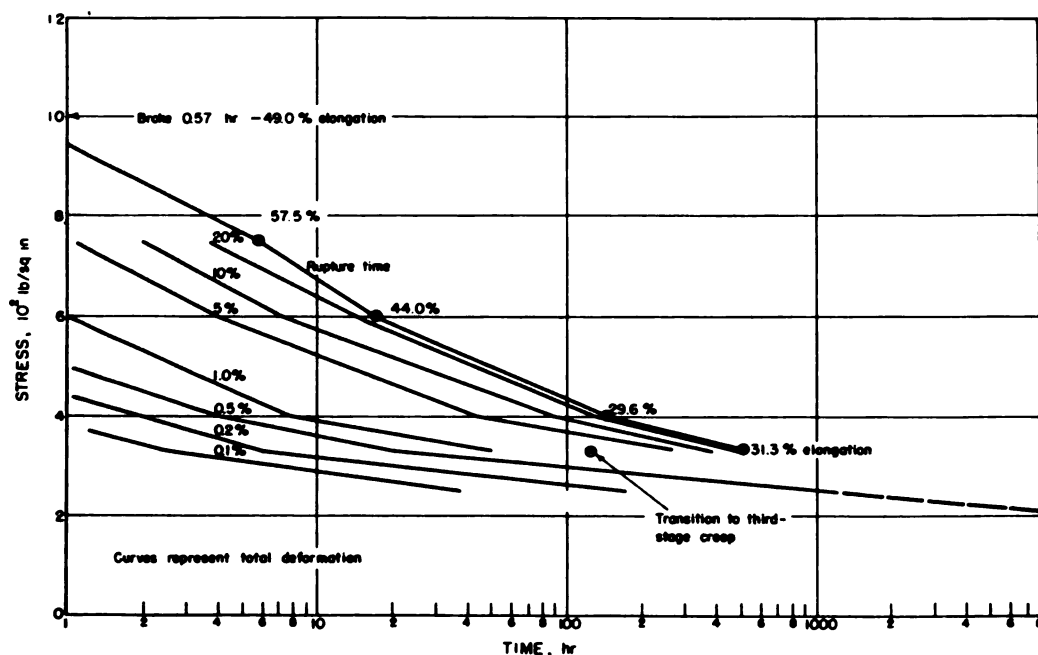


Fig. 1.2.7—Design Curves for 2S-O Aluminum Sheet at 450°C. Reprinted from W. F. Simmons and H. C. Cross, Creep of 2S-O Aluminum Sheet at 400° and 450°C, Battelle Memorial Institute, BMI-T-29, June 9, 1950.

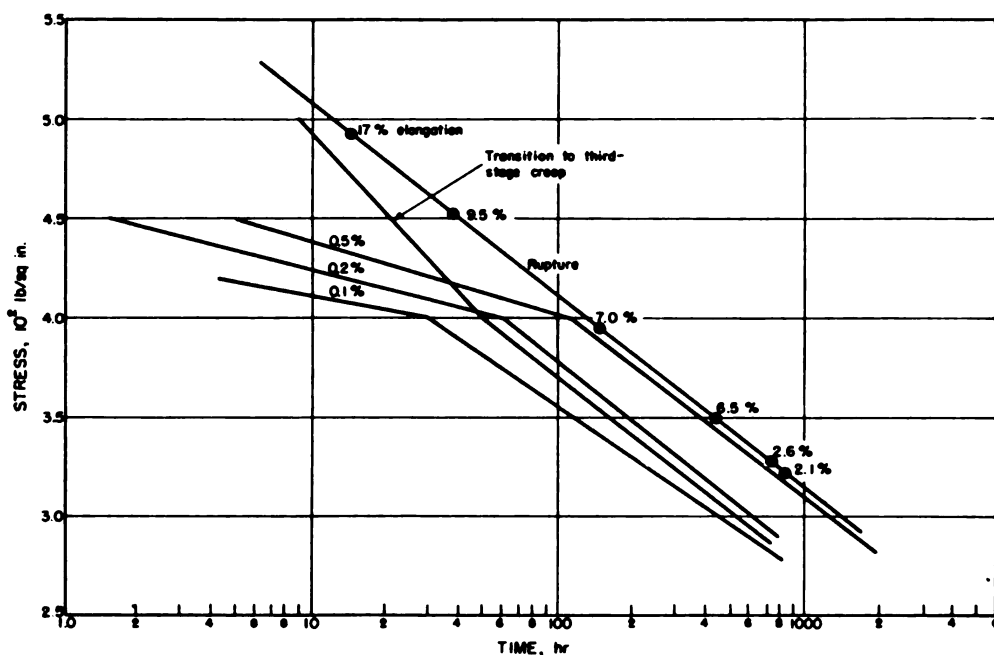


Fig. 1.2.8—Design Curves for 2S-O Aluminum Sheet at 500°C. Reprinted from J. A. Van Echo, W. F. Simmons and H. C. Cross, Creep of 2S-O Aluminum Sheet at 500° and 550°C, Battelle Memorial Institute, BMI-766, Sept. 11, 1952.

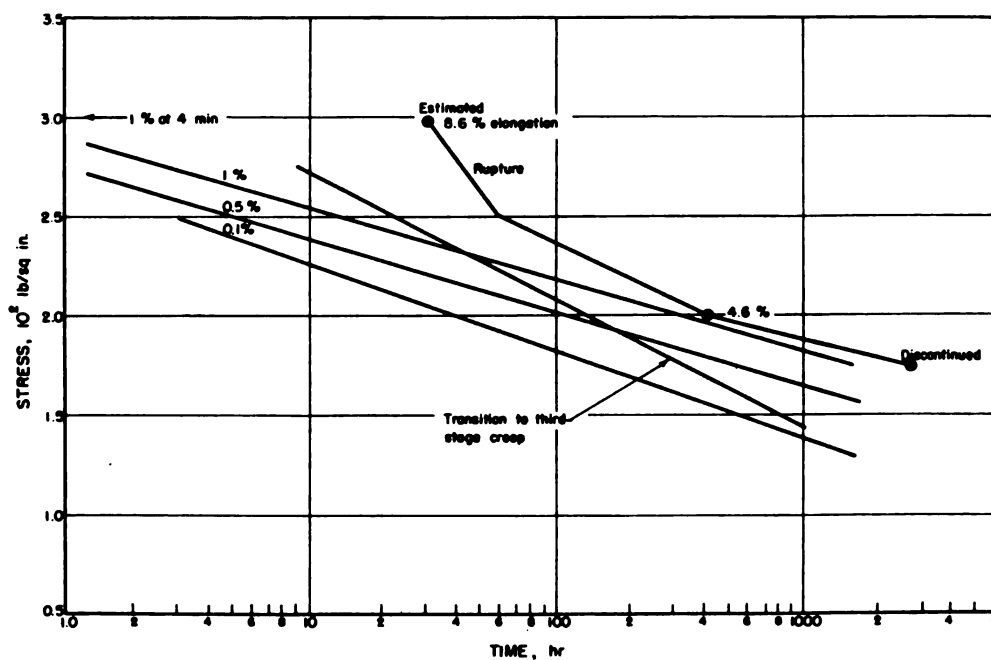


Fig. 1.2.9—Design Curves for 2S-O Aluminum Sheet at 550°C. Reprinted from J. A. Van Echo, W. F. Simmons and H. C. Cross, Creep of 2S-O Aluminum Sheet at 500° and 550°C, Battelle Memorial Institute, BMI-766, Sept. 11, 1952.

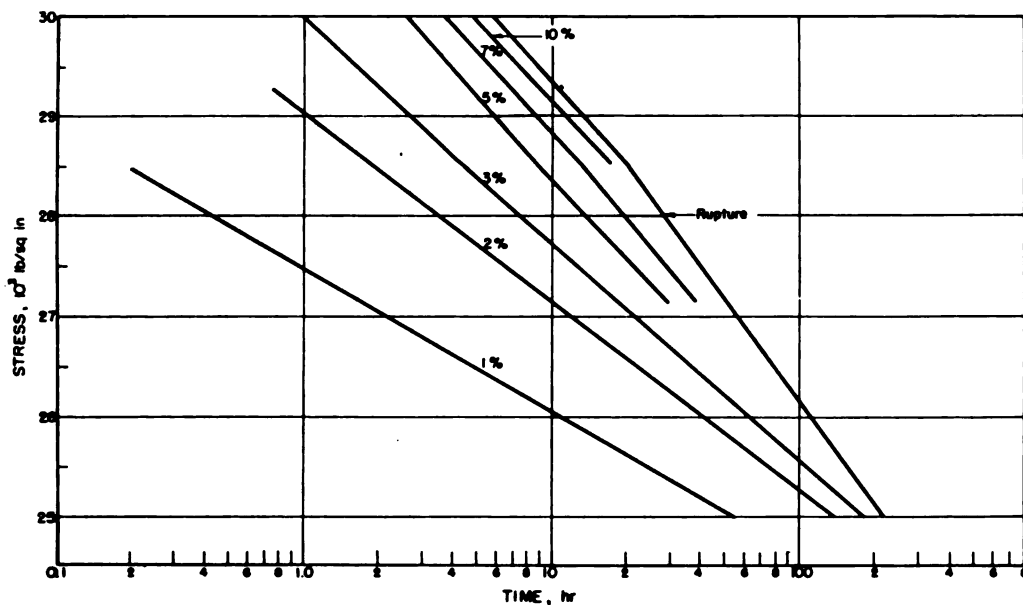


Fig. 1.2.10—Design Curves for Aluminum Alloy J-51S Sheet at 300°F, Tested in Longitudinal Direction. Reprinted from Progress on GE-ANP Project for March 1952, Battelle Memorial Institute, BMI-733, Apr. 1, 1952.

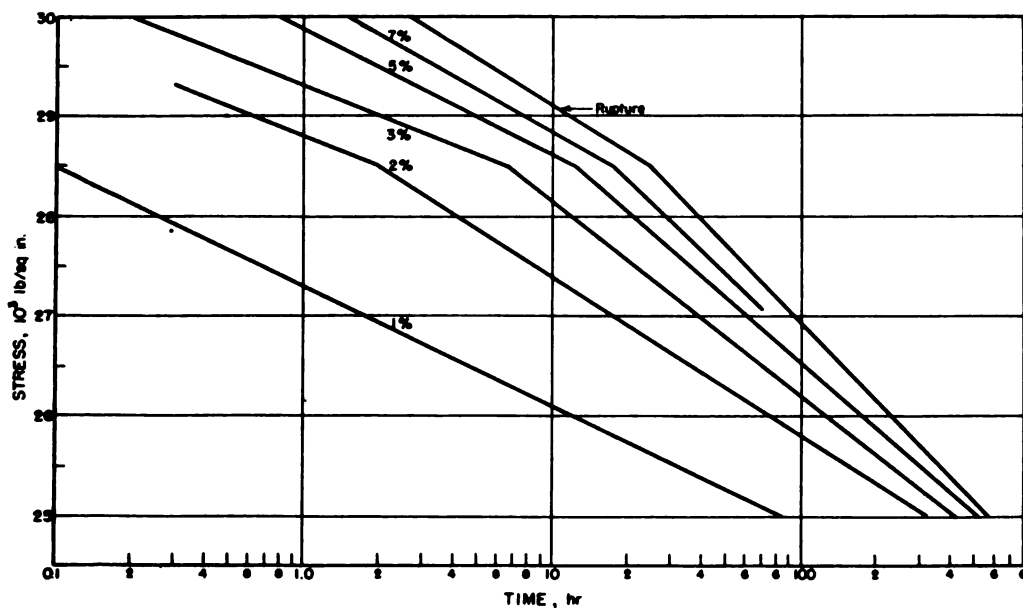


Fig. 1.2.11—Design Curves for Aluminum Alloy J-51S Sheet at 300°F, Tested in Transverse Direction. Reprinted from Progress on GE-ANP Project for March 1952, Battelle Memorial Institute, BMI-733, Apr. 1, 1952.

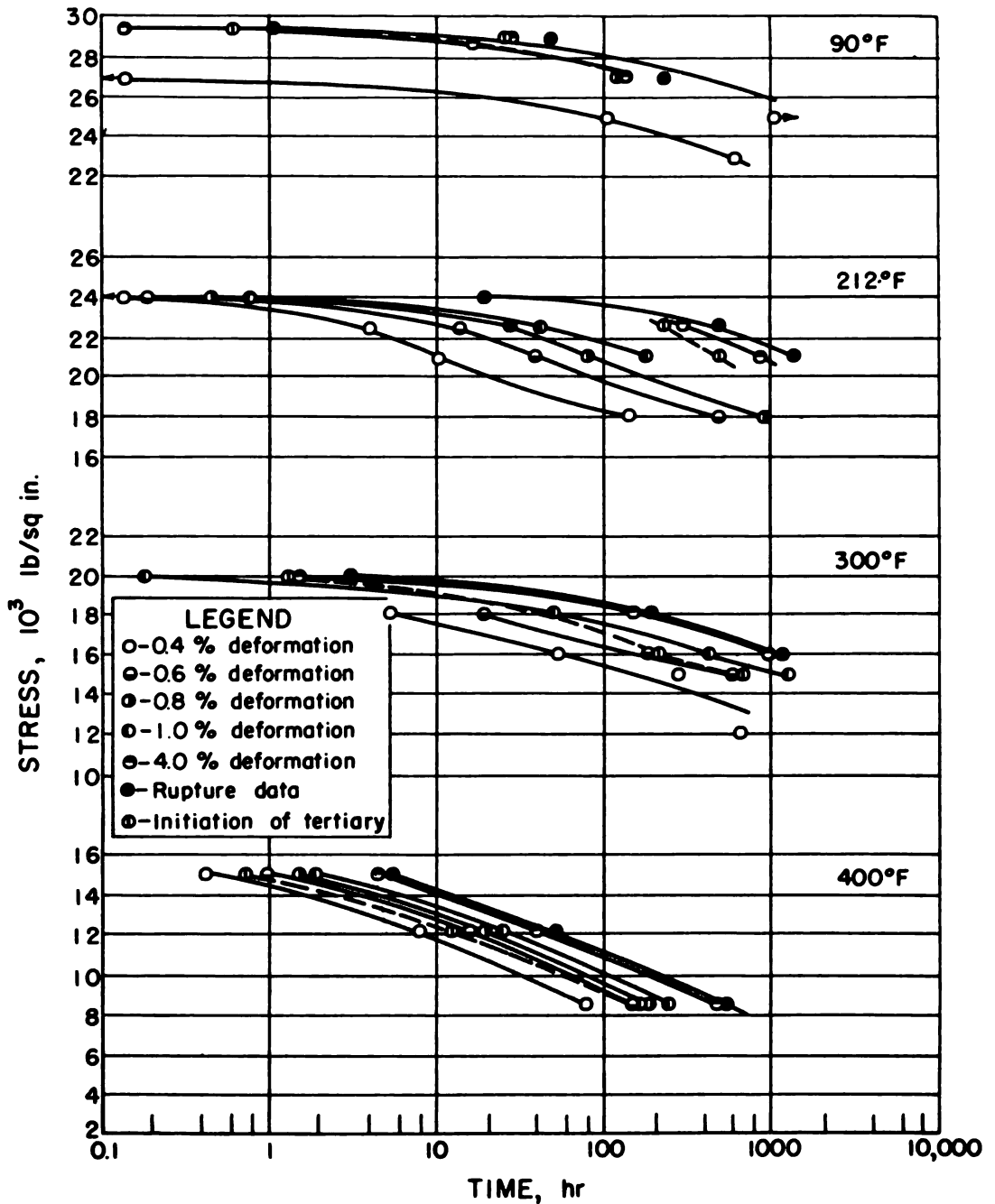


Fig. 1.2.12—Design Curves for Extruded 63S-T5 at 90°, 212°, 300°, and 400°F. Reprinted from O. D. Sherby and J. E. Dorn, Creep Properties of 63S Extruded Aluminum Alloy, A.S.T.M., Vol. 51, 1951.

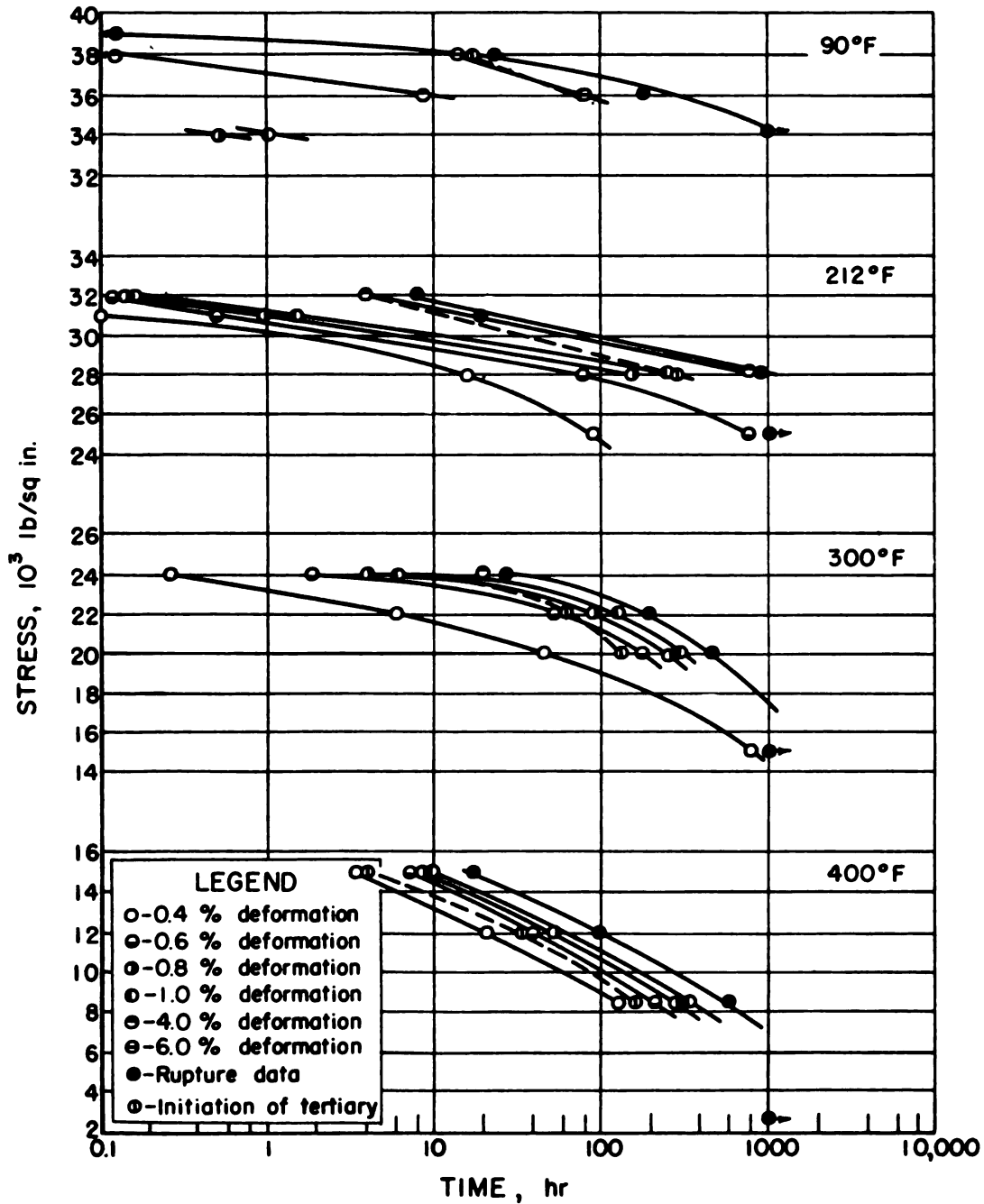


Fig. 1.2.13—Design Curves for Extruded 63S-T6 at 90°, 212°, 300°, and 400°F. Reprinted from O. D. Sherby and J. E. Dorn, Creep Properties of 63S Extruded Aluminum Alloy, A.S.T.M., Vol. 51.

Comparative fatigue strengths for some of the aluminum alloys at room temperature, 300°, 400°, and 500°F are shown in Fig. 1.2.14.

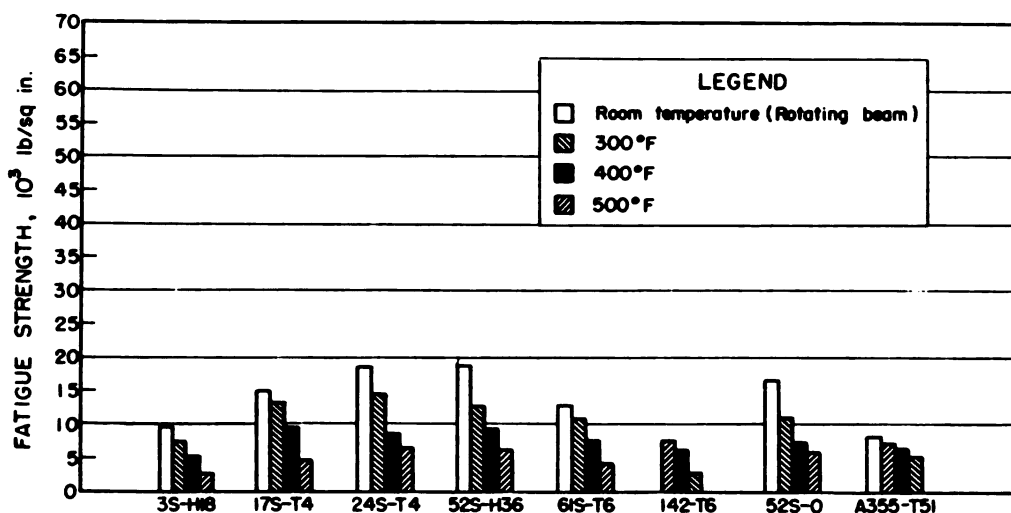


Fig. 1.2.14—Comparison of the Fatigue Strengths of Various Aluminum Alloys at 5×10^8 Cycles as Affected by Temperature. Constructed from aluminum producers data by Battelle Memorial Institute, Aug. 1, 1952. Tested after stabilization periods of 0.5 to 2 hr at testing temperature.

MELTING AND CASTING

The melting and casting of aluminum and its alloys is accomplished readily by conventional metal-processing techniques. Although electricity theoretically should offer advantages, in this country electricity has not been used very extensively as a source of power for melting aluminum. Melting is generally carried out in a fuel-fired furnace of either the direct- or indirect-flame type.

High-purity aluminum, because of its poor casting characteristics, is very seldom used for castings. Alloy additions are made to produce the commercially available alloys. Casting alloys of both the heat-treatable and non-heat-treatable types, covering a wide range of properties, are available.

Wrought alloys are produced from cast ingots, the size and shape of which depend on the end product and the manufacturing method.

FOUNDRY PRACTICE

Three major factors influence the quality of aluminum and aluminum alloy castings:

1. **The Affinity of Molten Aluminum for Gases.** Hydrogen is the common offender and may originate from water vapor in the atmosphere or hydrocarbon fumes from open flames. Hydrogen absorption results in pinhole porosity after solidification.

Various investigators have demonstrated that the solubility of hydrogen in solid aluminum is substantially zero. Hydrogen solubility in molten aluminum increases with increasing temperature, as shown in Table 1.2.7.

The rapid decrease in the solubility of hydrogen to practically zero during solidification causes precipitation and formation of pin holes. Fluxing the molten metal with chlorine,

Table 1.2.7—Solubility of Hydrogen in Aluminum

(From Gases in Light Alloys, L. W. Eastwood, John Wiley & Sons, Inc., 1946)

Temperature,* °F	Solubility, cc/100 gm, as determined by		
	Bircumshaw	Braun	Röntgen or Möllert†
1290	0.23	0.20	0.25
1470	.84	1.20	.95
1650	1.87	2.5	1.9
1830	3.87	4.3	3.5
2010	5.2
2190	7.2

* Pressure = approximately 1 atm

† With 3% copper, the solubilities are slightly lower

nitrogen, or aluminum chloride are treatments commonly employed to remove hydrogen.

2. Oxide Formation. Oxygen in the atmosphere reacts with molten aluminum to form aluminum oxide. Oxide inclusions in the metal produce unsound castings and reduce strength. Agitation and high temperatures accelerate the formation of oxide and must therefore be kept to a minimum. The inclusion of oxide may be reduced by fluxing the molten metal with chlorine, aluminum chloride, or nitrogen.

3. Foreign Contamination. This is a serious source of inferior-quality castings. Only clean equipment and proper use of protective coatings on tools and containers can correct this factor.

CASTING DESIGN CONSIDERATIONS

Some design factors, such as liberal radii, beading or ribs, uniform section thickness, and draft and shrinkage allowances, apply generally to all types of castings. On the other hand, characteristics inherent to a particular casting process may allow deviation from the general rules.

On sand castings, for instance, dimensional tolerances must be more liberal, at least $\pm \frac{1}{32}$ in. for thin sections and $\pm \frac{1}{16}$ in. for heavier sections; finish machining may be required to obtain closer tolerances.

In the case of die castings, the minimum wall thickness may be as low as 0.035 in. for small sections, depending upon the size and design of the casting as well as on the location of the section with respect to heavier adjacent sections.

FORMING AND FABRICATION

Most of the aluminum alloys can be readily formed cold. However, because of the wide range of properties, the degree of formability varies greatly with the alloy and temper.

The non-heat-treatable alloys covered in this report (2S, 3S, and 52S) work harden but have good forming qualities in the softer tempers. The heat-treatable alloys (17S, 24S, and 61S) can be readily formed in the annealed temper and are often worked in this state. Some work can be done after solution heat treatment and quenching, but the work must be performed before the accumulation of aging effects. Since aging is time- and temperature-dependent, forming and fabrication must be performed as quickly as possible after the quench. If necessary, the as-quenched material may be kept refrigerated for limited periods. Serious distortion may occur during quenching so that, whenever possible, the

heat-treated alloys should be solution treated before forming. The use of adequate jigs may reduce distortion should forming before heat treatment be necessary.

FORGING

The non-heat-treatable aluminum alloys are forged to some extent, but alloys with higher strength properties are usually desired in forgings. Therefore, the most common forging alloys are of the heat-treatable type, namely, 14S, 17S, 18S, 25S, and A51S.

Aluminum alloys have a tendency to be hot-short just below the melting point. This establishes a relatively narrow range within which forging must be completed. The best forging temperature for most alloys lies in the range between 750° and 900°F. The exact temperature depends, in each case, upon the alloy and the type of operation.

Forging dies for aluminum require more liberal corner and fillet radii than is necessary for steel. Even relatively wide ribs should have full radii rather than a flat section in the center. Aluminum forging dies also require a smoother surface than the dies used for forging steel, and all polishing marks should be in the direction of metal flow. Aluminum forging dies are usually preheated to 250° to 400°F and the first 50 to 100 blows with hammer dies should be light.

For hammer forging, the standard draft angle is 7°. For press forgings, there is no standard, but the common draft angle is 1° to 2°. Cold press forging is possible with aluminum alloys when little horizontal metal flow is required.

Lubricant, a mixture of high- and low-viscosity oils, is sprayed or swabbed on the dies during forging. Mineral, vegetable, or animal-base oils can be used as the high-viscosity oil and is mixed with a suitable solvent, in about a 50-50 proportion, for easier spreading.

SHEARING AND BLANKING

All alloys, regardless of temper, can be sheared in conventional equipment. Mechanical holdowns should have a clearance of about $\frac{1}{10}$ the sheet thickness. A low rake angle is recommended on the upper knife to reduce twist on thin stock.

Clearance for blanking tools is about 10 percent of the sheet thickness, for punching about 5 percent. Dies should taper about 0.75° from the cutting edge. Punches are generally annealed tool steel and the dies hardened tool steel. Band saws and routers are suitable for blank production.

BENDING

Bending is possible in brakes or with rolls by conventional methods. Equipment must be kept clean to avoid marring the surface. The radius required varies from 0 to 10 times the sheet thickness, depending upon alloy, temper, and thickness.

DRAWING

Equipment and tools are similar to those for drawing other metals. If successive draws are made without annealing, the amount of reduction per draw must be reduced progressively in the first steps. There is little change in hardness after the third draw. Radius on the die should be 4 to 15 times the metal thickness. Punch radius should be at least 4 times the metal thickness.

Dies and punches should be designed so that there is little change in metal thickness. This design factor is quite different from the practice with steel and brass, and tools designed for the latter are not likely to work with aluminum. Mineral oils are generally required for lubrication; soluble oils are not suitable. For severe draws a mixture of mutton tallow and paraffin is recommended.

FORMING

The Guerin process is widely used for forming and shallow drawing. A rubber pad serves as the die and, being confined in a steel pan, bends the work to the shape of the punch. It has the advantage, in addition to tooling economy, that spring-back can be compensated by tapering the sides of the punch so that the work is over-bent. Power hammers are also employed for forming and shallow drawing. The sheet can be shaped to the dies by a single blow or by a series of blows. Aluminum sheet is also formed in stretcher presses. This method is suitable for sweeping contours and causes little trouble from spring-back. When forming thin sheet in a press brake, the female die is sometimes lined with neoprene, or the sheet is covered with Scotch tape to prevent marking of the material.

SPINNING

Spinning, alone or in combination with drawing, is an economical method of producing parts. Pure aluminum and 2S can be spun cold to complicated shapes. Alloy 3S is widely used because of its higher yield strength but is not quite as easily formed as 2S. If 52S and/or the heat-treatable alloys are spun, they must be annealed frequently or heated with a torch before spinning. Beeswax, tallow, and petroleum jelly are suitable lubricants for most work. Large blanks can be lubricated with laundry soap.

MACHINING

Both wrought- and cast-aluminum alloys may be machined readily. However, conventional practices should be modified somewhat to obtain best results. For instance, tools for machining aluminum should have highly polished surfaces and be free from scratches as aluminum has a high coefficient of friction with steel.

The thermal expansion of aluminum is about twice that of steel—a good rule is 0.0001 in./in. of expansion for each 8°F. When dimensional accuracy is important, overheating is kept at a minimum with sharp, well-designed tools, a coolant, and feeds that are not too heavy. Even so it may be necessary to make a thermal allowance in measuring.

Standard tools are commonly used though tools for machining aluminum should be finished with considerably more side and top rake than those for cutting most other metals. The same applies to saws and files. Standard twist drills may be used though better results are usually obtained with drills having a larger spiral angle.

Lubricants should be applied copiously. A satisfactory cutting compound recommended for general use is a mixture of kerosene and lard oil. For milling, sawing, and drilling, economical soluble cutting oils may be used.

Most heat-treatable alloys contain a fairly high percentage of copper and can be machined to a good finish with or without lubrication. The non-heat-treatable alloys are easier to machine in full-hard temper as they tend to be gummy in the softer tempers.

Alloy 61S offers considerable resistance to tool penetration in the T-6 temper; however, by the use of properly prepared tools and good lubrication, fine finishes are obtainable with ordinary heavy cuts and feeds.

POWDER METALLURGY

Aside from refractory materials using aluminum and aluminum oxide mixtures, powder metallurgy methods are not generally associated with aluminum and its alloys. Some work has been done at Rensselaer Polytechnic Institute by Hall and Lenal using an electrical resistance sintering technique on compacts of iron particles in an aluminum matrix.

JOINING

RIVETING

Riveting is the oldest and most reliable method of joining stress-carrying parts of heat-treated aluminum alloy structures because no heat is involved and because riveting is well understood and highly developed. Too, modern riveting methods are largely independent of the operator's skill. Principles involved in designing riveted joints in aluminum and the actual riveting procedures are the same as for iron or steel.

Rivets and rivet wire are made in various aluminum alloys including 2S, 17S, 24S, and 61S. All but 2S rivets are used in the heat-treat condition and driven cold. Rivets in 17S and 24S are generally heat treated immediately before driving in order that they can be driven more easily. However, they may be stored under refrigeration for limited periods between solution treatment and driving time.

WELDING

The easiest welding alloy is 2S, but many other alloys are suitable for economical welds. Alloy 3S has almost as good welding characteristics as 2S and has higher properties. For still higher strength, alloy 52S is used, especially for resistance welding. Alloy 61S is widely employed where structural strength is important and the work can be heat treated after welding; this alloy may be welded by gas or resistance methods. Alloys containing copper, such as 17S and 24S, are suited to resistance welding.

GAS WELDING

Equally good results are obtained with oxyhydrogen or oxyacetylene flames. The flame is adjusted with a larger tip for hydrogen than for acetylene, and a neutral or slightly reducing flame gives best results with speed and economy. Surfaces should be clean of grease, oil, and dirt. When the surface is heavily oxidized, etching may be required, but cleaning with a wire brush is generally sufficient. In all gas welding processes, a liberal application of welding flux must be used to break down the oxide coating. It is very important to remove all of the flux after welding in order to prevent corrosion.

ARC WELDING

Most arc welding is done with coated electrodes of 2S or the 5-percent-silicon alloy (43S). Sheet less than $\frac{1}{4}$ in. thick is not usually arc welded. Operators accustomed to welding steel will require some practice with aluminum. One difference is that the arc is struck by a motion similar to that of striking a match. Touching the work directly will usually result in the rod and work freezing together.

Conventional equipment is used with reverse polarity (electrode positive). Carbon-arc welding produces welds of equal soundness with considerably less distortion than metal-arc welding and may be either manual or automatic. The electrode in carbon-arc welding is negative, but settings are similar to those employed in metal-arc welding. In both types of welding, the filler rod is fed in a manner similar to gas welding.

Shielded-arc welding, first developed for magnesium, is being used increasingly in recent years. It employs a tungsten electrode, a filler rod, and an inert shield of argon or helium gas. This method is especially good for alloy 52S. Atomic hydrogen welding (arc between two tungsten electrodes in an atmosphere of hydrogen) gives high welding speeds with good results.

Development work on the argon arc-process for closing the 2S aluminum-coated slugs demonstrated that this welding process is very sensitive to impurities in the argon gas.

The argon gas eventually produced for this purpose contains 99.8 percent argon, 0.2 percent nitrogen, less than 75 ppm of hydrogen, and less than 100 ppm of oxygen. The use of high-frequency initiation of the arc necessitated the development of a welding torch with insulation which will not break down as readily as that in commercially available torches.

RESISTANCE WELDING

Spot welding is possible with either a. c. (single-phase or three-phase), magnetic energy-storage, or condenser or battery energy-storage equipment. The a. c. equipment is widely used and is cheaper; however, the stored-energy equipment gives better surface finish. High currents and short times are required. Dome tips are customary, but one flat tip can be used when necessary. The flat tip, if used, should be on the heavy electrode. Seam welds with roll-type electrodes have been used successfully to produce continuous or intermittent seams.

Flash welding to produce butt or miter welds is another satisfactory method. With proper machine and die design, high flash welding rates can be obtained.

BRAZING

Brazing is distinguished from welding in that it employs a filler metal which melts at a temperature slightly below that of the parent metal, and the joint is made without melting the aluminum alloy to be joined. Unlike soldering, where the joint is made at relatively low temperatures by the use of a heavy-metal filler alloy, the brazing alloy is predominantly aluminum alloyed with sufficient silicon, or silicon and copper, to give an alloy having the desired melting point. The filler alloy has the characteristic corrosion resistance of an aluminum alloy.

Brazing techniques have been developed for torch-, furnace-, and dip-brazing of alloys 2S, 3S, and 61S. No satisfactory techniques are available for the high-strength alloys such as 17S or 24S. Brazing is cheaper than welding and produces neater joints requiring less finishing. Material too thin to weld may be brazed satisfactorily. Like welding, the process requires special fluxes and filler materials. Joints must be designed more carefully than in welding, so that the molten filler alloy will flow under the force of capillarity. Lock seam, tee, square butt, and lap joints, with sufficient clearance for the filler to flow, are generally used rather than scarfed butt joints. Brazing sheet, consisting of the base alloy with 5 to 10 percent of filler on one or both sides of the sheet, is available. Use of this sheet eliminates the need for a separate filler alloy in making the joint.

The most important characteristic of brazing is the flow of the molten brazing alloy into the joint under the influence of capillary action. The presence of grease, dirt, and oxide film profoundly affects the surface tension of the molten filler alloy. It is essential that all grease and dirt be removed by solvent or etching-type cleaners, and that a flux, capable of rapidly dissolving the oxide and wetting the metal surface, be employed.

Temperatures for brazing range from 1060° to 1185°F, depending upon the alloy, the design of the joint, and the filler material used. Since the brazing temperatures of aluminum are above its annealing temperature, work-hardened alloys after brazing will have the properties characteristic of the annealed state. Alloy 61S may be solution heat treated to improve the properties by quenching directly from the brazing operation or, where the design of the joint is such that breakage occurs when directly quenched, it may be subsequently heat treated and aged to develop the properties of the heat-treated tempers. Brazed joints in the common alloys will develop strengths equivalent to the annealed properties of these alloys.

Removal of the flux following brazing is essential in order to prevent serious corrosion. Many parts can be immersed in boiling water directly after completion of the brazing operation to remove the bulk of the flux, or they can be immersed in boiling water after

cooling from the brazing heat. Following the treatment in hot water, a dip in concentrated nitric acid for 5 to 10 min is recommended followed by a second rinse in boiling water.

SOLDERING

Soldering as a method of joining aluminum is quite satisfactory as long as the joints are dry and not subject to corrosive conditions. Where moisture is present to act as an electrolyte, the difference in potential between the solder and the aluminum alloy may cause electrolytic corrosion and failure of the joint. Therefore, soldering is not recommended for joints exposed to the weather.

In soldering, oxide is removed from the parts by wire brushing or with a flux. An ordinary soldering iron, tinned with a lead-tin solder, will remove oxide and permit welding of the aluminum solder and the part. Special noncorrosive aluminum fluxes and solders are available for joining aluminum parts.

It should be noted that even the best aluminum solders have comparatively low mechanical properties, and the joint design strength should be supported by crimping, interlocking, riveting, bolting, or similar means.

RESIN BONDING

All of the aluminum alloys can be joined by adhesives, and this method is especially suitable where large lap joints are required. Thermoplastic, thermosetting, and vulcanizable bonds are among the types of resin bonds that can be produced.

HEAT TREATMENT

Aluminum and aluminum alloys are similar to many other nonferrous alloys in the sense that they may be divided into two groups; the "non-heat-treatable" alloys, and the "heat-treatable" alloys.

The "common" or "non-heat-treatable" wrought alloys contain elements that remain substantially in solid solution at all temperatures or form constituents that are insoluble. Included in this group are the alloys 2S, 3S, and 52S. The strengths of these alloys depend on the amount of cold work introduced after the last annealing operation. Six tempers are available ranging from the soft or annealed temper, designated by the symbol "O," to the full hard temper, designated as H18 in 2S and 3S. The intermediate tempers in 2S and 3S are designated: "H12" for the $\frac{1}{4}$ -hard temper, "H14" for the $\frac{1}{2}$ -hard temper, and "H16" for the $\frac{3}{4}$ -hard temper.

For 52S, the cold worked tempers are stabilized by a low-temperature thermal treatment. To show the use of a thermal treatment following cold working, the temper designations H32, H34, H36 and H38 are used to denote the $\frac{1}{4}$ -hard, the $\frac{1}{2}$ -hard, the $\frac{3}{4}$ -hard, and the full-hard tempers, respectively.

The "heat-treatable" wrought alloys 17S, 24S, 61S, and 63S contain elements or constituents that have considerable solid solubility at elevated temperatures and restricted solid solubility at lower temperatures. The treatment used to bring about solution is known as "solution heat treatment" and is achieved by heating at an elevated temperature for a specified length of time, depending on the alloy and sheet thickness, followed by a rapid quench in water. In this state the alloy is unstable, and the properties gradually increase as precipitation or "aging" proceeds. Attainment of stability and maximum properties with some alloys can be accelerated by furnace aging for some hours at 240°–380°F. This treatment is known as "aging" or "precipitation hardening."

Tables 1.2.8 and 1.2.9 list the recommended heat-treating and annealing practices for selected wrought alloys. Table 1.2.10 gives heat-treating data for selected casting alloys. Cold work may be used after solution heat-treatment as an additional operation which

substantially increases the yield strength but with loss in ductility or formability. Many combinations of heat treatment, cold work and aging are possible. The chief temper designations are listed below.

Temper Designations for Heat Treated Aluminum Alloys

T2	Annealed
T3	Solution heat-treatment and then cold work
T4	Solution heat-treatment and natural aged to a substantially stable condition
T5	Artificially aged only
T6	Solution heat-treatment and then artificially aged
T7	Solution heat-treatment and then stabilized
T8	Solution heat-treatment, cold worked, and then artificially aged
T9	Solution heat-treatment, artificially aged, and then cold worked
T10	Artificially aged and then cold worked.

For a detailed discussion of the temper designations of aluminum alloys the reader is referred to aluminum data books available from the major aluminum producers.

CORROSION BEHAVIOR

AIR AND WATER

The relative corrosion resistance of selected aluminum alloys to atmospheric and sea-water corrosion is given in Table 1.2.11. Of the wrought alloys, commercially pure aluminum, 2S, is highly resistant to corrosion. The alloys 3S and 52S, 61S and 63S in which the principal alloying ingredients are either manganese, magnesium, chromium, or magnesium and silicon in ratios to form Mg_2Si , show very little corrosion under atmospheric or marine exposure. Similarly, the casting alloys containing silicon and/or magnesium are the most resistant. The copper-containing alloys, whether in cast or wrought form, are less resistant.

When the decision to attempt water cooling the Hanford pile was reached in February 1943, aluminum was given serious consideration because of its excellent corrosion resistance and good thermal characteristics. The exploratory corrosion studies resulting from this decision have been described by R. B. Hoxeng.* Among the variables investigated for 2S aluminum were the effects of pH, temperature and pH, flow-rate of solution, chloridation, hydrogen peroxide, radiation, calgon, nitrite and nitrate ion, dichromate ion as an inhibitor.

It has been demonstrated that the pH of the water is an important factor. The corrosion rate increases markedly below a pH of about 4.5 and somewhere above a pH of 7. As the pH of the solution is lowered, pitting becomes noticeable around pH 5.5 and becomes serious at a pH of 4.0 or below. It has been shown that the corrosion rate increases with increasing temperature.

For solutions in the pH range 4.5 to 7, the corrosion rate is low and for the most part independent of the flow rate. Very small amounts of chloride ion are undesirable. The results of the various investigations on the effect of small amounts of hydrogen peroxide ($10^{-6}N$ to $10^{-4}N$) do not give a consistent picture. Similarly, inconsistent results have been obtained in studies of the effect of dissolved silica.

* National Nuclear Energy Series, IV, Vol. 6A, Chapter 12, page 221, 1951.

Table 1.2.8—Typical Heat-treating Cycles for Some Wrought Aluminum Alloys

Alloy	Solution heat treatment			Precipitation treatment (aging)		
	Soaking temp., °F	Quench	Temper* designation	Aging temp., °F	Aging time, hr	Temper designation
17S	930-950	Cold water	T4
24S	910-930	Cold water	T4	375 ± 5†	12	T81
				375 ± 5†	9	T86
61S	900-900	Cold water	T4	320 ± 5	18	T6
				350 ± 5	8	T6
63S	350 ± 5	4	T5
	900-900	Cold water	T4	350 ± 5	8	T6

* In the stable condition

† Cold working subsequent to solution heat treatment and prior to the precipitation treatment is necessary to obtain the desired properties

Table 1.2.9—Typical Annealing Cycles for Some Wrought Aluminum Alloys

Alloy	To soften after heat treatment			To remove cold work		
	Soaking temp., °F	Soaking time, hr	Cooling rate*	Soaking temp., °F	Soaking time, hr	Cooling rate*
2S		Not heat treatable		650 ± 15	½-2	A or B
3S		Not heat treatable		750 ± 15	½-2	A or B
17S	775 ± 25	2	B	650 ± 10	2	A
24S	775 ± 25	2	B	650 ± 10	2	A
52S		Not heat treatable		650 ± 10	2	A or B
61S	775 ± 24	2	B	650 ± 10	2	A or B

* Cooling rates from annealing temperature:

A—Air cool

B—Furnace cool, 50°F/hr to 500°F

Table 1.2.10—Typical Heat Treatments for Some Aluminum Sand Castings

Alloy and heat treatment	Solution heat treatment			Artificial aging treatment	
	Time, hr*	Temp., °F†	Quench‡	Time, hr§	Temp., °F†
122-T2	2-4	600
122-T61	12	950	Water	10-12	310
142-T21	2-4	650
142-T77	6	970	Still air	1-3	650
356-T51	7-9	440
356-T6	12	1000	Water	2-5	310
356-T7	12	1000	Water	7-9	440
356-T71	12	1000	Water	2-4	475

* Soaking time, after load has reached specified temperature, required for average casting. Time can be decreased or may have to be increased, depending upon particular castings, as demonstrated by experience

† Temperature setting for control instrument. Variation of temperature in furnace should not exceed ± 10°F

‡ Water temperature from 150° to 212°F can be employed; boiling water recommended since it minimizes quenching stresses and distortion

§ Exact time required influenced by foundry variables; select on basis of obtaining typical hardness values

Table 1.2.11—Relative Resistance of Aluminum Alloys to Corrosion

Aluminum Alloys	Ratings*			
	Outdoor Atmospheres			
	Rural†	Industrial‡	Marine§	Sea Water¶
2S	A+	A	A	A
3S	A+	A	A	A
17S	A	B	C	C
24S	A	B	C	C
52S	A+	A	A	A
61S	A	A	B	B
63S	A+	A	A	A
13	A	A	B	B
43	A	A	B	B
122	A	B	C	C
142	A	B	C	C
214	A+	A	A	A
218	A+	A	A	A
220	A+	A	A	A
356	A	A	B	B
360	A	A	B	B

* Ratings in all columns are interrelated. An "A" rating is highest. Rating compares the stability of alloys as a group. However, under many conditions, alloys rated "C" are used with satisfactory results; on the other hand, alloys rated "A" or "B" may require protection under certain exposure conditions

† Inland and uncontaminated by industrial smoke and fumes

‡ Contaminated by smoke and industrial fumes

§ Frequent salt mist

¶ Immersion in salt water; pure aluminum and alloys containing magnesium or magnesium and silicon (and not copper) as the major alloying constituents demonstrate good resistance to corrosion by unpolluted sea water

Sodium hexametaphosphate ("Calgon") when used as an inhibitor increases the corrosion rate. Various tests in the presence of nitrite and nitrate ion as inhibitors yield inconsistent results. However, dichromate ion is most effective in reducing the corrosion.

Results of corrosion tests on other aluminum alloys (i.e., the wrought alloys 72S, 52S, and 61S and the die casting alloys 360 and 360 A) as well as on galvanic couples of aluminum in contact with other metals are discussed in considerable detail in the previously noted reference.

CHARACTERISTICS OF ALUMINUM AS A LIQUID METAL

Aluminum offers no advantage in liquid metal applications over the lower-melting metals, such as bismuth, tin, mercury, cadmium, and lead. Above 1220°F, almost all metals are attacked and thus long-time contact with other metals at elevated temperatures is not feasible. Melting pots for aluminum utilize metallic oxide coatings, but, of course, this would not be suitable under dynamic conditions where thermal stress is important. Generally, gray cast iron is a better container metal for liquid aluminum than low-carbon steels, Armco iron, or the stainless type steels.

Aluminum is very susceptible to oxidation. The molten metal forms a thin oxide blanket which remains passive until broken by agitation. Finely divided aluminum will burn with explosive violence if ignited in air and has been observed to burn in nitrogen. Hot liquid

aluminum at high temperature will react with H_2O to form the oxide and release highly explosive hydrogen.

OTHER MEDIA

The corrosion resistance of aluminum to certain inorganic and organic reagents is listed in Table 1.2.12.

PROTECTIVE TECHNIQUES

Aluminum's resistance to corrosion is generally sufficient for many applications without additional protection. However, protective coatings and finishes may be desirable for some alloys which have markedly poorer corrosion resistance than pure aluminum.

CLEANING

A necessary prerequisite to any finishing method is proper cleaning of the surface. In fact, cleaning is often desirable even when no finish is to be applied. Wax and grease present after fabrication are most likely to cause trouble if not removed. Among the most common methods of cleaning are vapor degreasing, acid or alkaline dip, and emulsion cleaning.

MECHANICAL FINISHING

Since highly polished surfaces in many cases impart increased resistance to corrosion, a summary of mechanical finishing techniques is shown in Table 1.2.13.

CHEMICAL FINISHES

By simple dip or etching processes, it is possible to obtain various degrees of surface preparation. Processes that fit this category are known under such patented names as Alodine, Alrok, Bonderite 170, and many others. Chemical surface treatments are not often used directly as a protective finish but are more commonly employed as preparation for painting, enamelling, or organic finishes.

ELECTROLYTIC OXIDE FINISHES

Various types of anodic coatings appear in this group, some of which lend themselves to the production of colored films directly from the electrolyte. Among the patented processes are Alumilite, Alzak, and Brytal.

The anodizing process uses the aluminum part as the anode in an electrolyte, such as a dilute solution of sulfuric, chromic, oxalic, or boric acid. The types of oxide coatings obtained vary in their characteristics and depend upon the electrolyte, the temperature, the time, and the voltage used in anodizing. In general, anodized coatings increase resistance to corrosion and abrasion.

ELECTROPLATED FINISHES

Aluminum can be satisfactorily electroplated, but the natural oxide film must be replaced with a tightly adhering coat of zinc. This is accomplished by immersion in a zincate solution. Brass, zinc, and cadmium can be plated on aluminum with this zinc undercoat directly from cyanide solutions. Chromium, copper, and the precious metals are usually deposited on an undercoat of nickel, which in turn is deposited on the zinc coating.

Table 1.2.12—Action of Some Chemicals on Aluminum Alloys

(Reprinted from Reynolds Aluminum Data Book)

Reagent	Recommended use*		
Inorganic acids			
Boric acid solutions, 1-5%	A
Chromic acid (pure), any concentration	...	B	...
Hydrochloric acid	X
Hydrofluoric acid, 1-60%	X
Nitric acid	...	B	...
Phosphoric acid	X
Sulfuric acid	...	B	...
Sulfurous acid	...	B	...
Metal salts and hydroxides			
Acid Salts	...	B	...
Alkali metal bicarbonates	A
Alkali metal carbonates (any concentration)	X
Alkali metal hydroxides (any concentration)	X
Arsenates (any concentration)	...	B	...
Borax solutions, 1-5%	...	B	...
Bromides	X
Chlorides (all)	X
Chromates (most), any concentration	...	B	...
Fulminate of mercury	X
Heavy metal salts (most)	X
Hydroxides (most), any concentration	X
Iodides	X
Mercury salts	X
Nitrates (all)	...	B	...
Permanganates (most), any concentration	A
Phosphates (most), any concentration	X
Potassium hydroxide, any concentration	X
Potassium nitride	A
Salt (sodium chloride)	...	B	...
Sodium hydroxide (any concentration)	X
Sodium silicate (water glass), any concentration	...	B	...
Sulfates	A
Water			
Sea Water, 100%	...	B	...
Steam, 100%	A
Carbonated	A
Chlorinated	X
Distilled	A
Rain	A
Tap, 100%	...	B	...
Miscellaneous			
Air	...	B	...
Bleaching solutions	X
Fluorine	X
Hydrogen peroxide, 3-30%	...	B	...
Hydrogen sulfide	A
ink (iron), 100%	...	B	...
Mercury	X
Nitrous gases 100%	...	B	...
Oxygen	A
Sulfur	A
Sulfur dioxide	A

*"A" — aluminum is not seriously affected by the chemical in question at ordinary temperatures and in the absence of complicating factors, such as corrosive impurities in the chemical or galvanic action resulting from contact with dissimilar metals; "B" — aluminum should not be used without further tests or additional data; "X" — aluminum will not normally be satisfactory unless there are special circumstances and, in any event, should not be used without rather complete additional testing. Rating the action of various chemicals on aluminum has certain objections, since minor changes in composition of the chemicals or operating conditions can greatly affect corrosion rates. For example, impurities, known or unknown, in the chemicals involved may cause corrosion. Before any substantial application is undertaken, a trial should be made. In some cases, the application of a suitable protective coating permits the use of aluminum in contact with materials which might attack the bare metal. Where aluminum is recommended, "A," or where trial is warranted, "B," the recommendation applies to 100% concentration of the reagent unless otherwise indicated. Where aluminum is not recommended, "X," the recommendation applies to any concentration of the reagent

Table 1.2.13 — Mechanical Finishing of Aluminum Alloys

	Solid wheel	Roughing cloth belt	Sewed muslin	Greasing or oiling	Buffing	Coloring	Finish grinding*
Abrasive	Al ₂ O ₃ or SiC	Al ₂ O ₃	Al ₂ O ₃	Turkish emery	Tripoli	Fine lime or soft silica	SiC
Carrier	Solid wheel	Cloth belt	Sewed muslin	Sewed muslin	Pocketed muslin	Open muslin or flannel	Solid wheel
Grit	16 to 100	46 to 300	buffs	buffs	buffs	...	30 to 40
Bond	Phenolic resin	Glue	46 to 48	120 to 240	Vitrified
Hardness	Medium	...	Glue	Glue	Soft
Peripheral speed of wheel, ft/min	6000 to 12000	...	Medium	Medium	Soft	Very soft	6000 to 7000
Lubricant	Dry or grease	Grease or kerosene	Grease	Grease	Grease	3000 to 4000	Soluble oil, 1 to 35 or 40

* Mechanical finish applied to castings—to be preceded by machining

ORGANIC FINISHES

All common coatings, such as lacquers, enamels, varnishes, paints, and porcelainized finishes, are used without special precautions, although cleaning is important. In some cases where additional protection is desired, chemical or electrochemical pretreatments may be employed. The organic finishes are applied by almost any method including: brushing, spraying, dipping, or roll coating. Aluminum and zinc chromate paints are excellent primers for paint and enamel, but are not suitable for all lacquer finishes. Primers containing lead are not recommended.

CLADDING

It is often advantageous to use high-strength aluminum alloy sheet, plate, and wire, but since most of the stronger aluminum alloys have lowered resistance to corrosion, these alloys are often clad with a thin layer of high-purity aluminum. This cladding not only protects the surface against corrosion but provides electrolytic protection on sheared edges or where the cladding may have become scratched. Clad products are produced by composite hot rolling and conventional cold finishing.

METALLOGRAPHY

The methods used in mounting aluminum specimens for microscopic examination are no different than those used for other metals. In grinding and polishing, however, greater care must be practiced to prevent flowed metal and scratches. Successful polishing is aided by the use of emery papers that have been coated with a mixture of paraffin and kerosene. This minimizes the tendency for foreign particles to become embedded in the specimen.

Etching for microscopic examination is successful with any number of general purpose etchants, such as dilute hydrofluoric acid, sodium hydroxide, or Keller's etch. For constituent identification, there are selective etching solutions, which are described in the ASM Metals Handbook in the section on "Metallography of Aluminum Alloys."

Treatment of aluminum for macroscopic analysis is simple. Often a smooth saw cut prior to etching will readily reveal defects such as cracks, inclusions, folds, and seams. Most generally used etchants include sodium hydroxide followed by a nitric acid rinse, aqua regia, or Tucker's etch.

CONSTITUTIONAL DIAGRAMS

One of the most complete bibliographies on Aluminum Alloy Systems is found in the ASM Metals Handbook, 1948 edition. A very comprehensive discussion is contained in this Handbook complete with constitutional diagrams of the better-known systems. Another excellent reference on phase diagrams is the ASM publication, "Physical Metallurgy of Aluminum Alloys." For historical background, the reader should refer to the extensive bibliography contained in "The Aluminum Industry," Volume II, by Edwards, Frary, and Jefferies.

SELECTED READING LIST*

Battelle Memorial Institute, J. A. Van Echo, W. F. Simmons, and H. C. Cross, BMI-786, Sept. 11, 1962 (classified).

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LIQUID METALS HANDBOOK, Atomic Energy Commission, Department of the Navy, R. N. Lyons et al., NAVEXOS, P 733, 188 pp, June 1, 1950.

PHYSICAL METALLURGY OF ALUMINUM ALLOYS, W. L. Fink, F. Keller, W. E. Sicha, J. A. Noda, Jr., and E. H. Dix, Jr., American Society for Metals, Cleveland, Ohio, 1949.

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AN APPRAISAL OF THE USEFULNESS OF ALUMINUM AND ALUMINUM ALLOYS FOR SUPERSONIC AIRCRAFT AND GUIDED MISSILE CONSTRUCTION, The Rand Corporation, C. M. Craighead, L. W. Eastwood, and C. H. Long, R104, 240 pp, August 8, 1948.

THE ALUMINUM INDUSTRY, J. D. Edwards, F. C. Pray and Zay Jefferies, McGraw-Hill, New York, New York, 1930.

*Data books on aluminum alloys, their fabrication and heat treatment are available upon request from the principal producers: the Aluminum Company of America, Reynolds Metals Company and the Kaiser Aluminum Company.

CHAPTER 1.3

Beryllia

R. E. Long and H. Z. Schofield

REACTOR APPLICATION

The oxide of beryllium has refractory and nuclear properties which make it interesting for use as a structural material for fuel elements, a reflector, or a moderator for a high-temperature nuclear reactor. The classical example of beryllia applied to reactor design is the Daniels Pile. In this high-temperature pile, beryllia was proposed for the moderator, fuel elements, and portions of the reflector. Beryllia is also being used as a reflector in the Bulk Shielding Facility.

Although it has desirable nuclear properties, beryllia, like other ceramics, is brittle. It has better resistance to thermal shock than most other ceramic materials and a higher melting point than any metal except tungsten, molybdenum, tantalum, rhenium, or osmium. It is a good electrical insulator at elevated temperatures.

OCCURRENCE AND PRODUCTION

The occurrence, production, and extraction of beryllia are described in Chap. 1.4, "Beryllium and Its Alloys." In one production method for processing beryl ore into beryllium metal, beryllium hydroxide is formed. At this point in the process, if beryllia is desired, the hydroxide is dissolved in H_2SO_4 , and the resulting beryllium sulfate can be crystallized to form a higher purity beryllium sulfate. The sulfate is then calcined to a ceramic grade of beryllia (BeO). The current price of ceramic-grade beryllia powder is \$8 to \$11/lb. A fused grade is priced at \$10 to \$12/lb.

An "ultrapure" beryllia has been prepared starting with the metal or a salt, preferably the sulfate, which is then converted to beryllium basic acetate, $BeO \cdot 3Be(C_2H_3O_2)_2$. A chloroform solution of this material is extracted with redistilled water. This is dried and distilled several times from quartz flasks. The distilled basic acetate is fumed down with H_2SO_4 , and the resulting sulfate is converted to oxide by igniting at $1000^\circ C$.

PHYSICAL AND CHEMICAL CONSTANTS

Table 1.3.1 gives selected physical and chemical constants of beryllia.

CRYSTALLOGRAPHY

Beryllia crystallizes in the hexagonal system with a zincite (ZnO) type of structure. It is prismatic with a definite 1010 cleavage. Beryllia is an ionic crystal consisting of a

Table 1.3.1 — Physical and Chemical Constants of Beryllia

Density,* gm/cm ³	
Single crystal	3.025
Hot pressed	2.6–2.95
Slip castings after firing	2.2–2.8
Dust pressings after firing	2.2–2.8
Melting point, °C	2550 ± 25
Boiling point, °C	4260 ± 160
Heat of fusion, cal/mole	17,000 ± 1400
Entropy of fusion, cal/(mole)(°C)	6.0 ± 0.5
Heat of vaporization, cal/mole	117,000 ± 10,500
Entropy of vaporization, cal/(mole)(°C)	25.8 ± 2.3
Heat of sublimation, cal/mole	
600 to 3000°C	152,000 ± 10,000
Heat of formation, $\Delta H_{f25^\circ\text{C}}^\circ$, kcal	–149.0
Standard free energy change of formation, $\Delta F_{f25^\circ\text{C}}^\circ$, kcal	–139.0
Thermal conductivity†	
Specific heat,‡ cal/(mole)(°C)	
–273°C	0
–100°C	0.3
0°C	5.5
100°C	7.7
400°C	10.5
800°C	12.3
Enthalpy ($H_T - H_{25^\circ\text{C}}$), cal/mole	
127°C	730
327°C	2540
527°C	4700
727°C	7010
927°C	9510
Entropy ($S_T - S_{25^\circ\text{C}}$), cal/(mole)(°C)	
127°C	2.09
327°C	5.73
527°C	8.83
727°C	11.40
927°C	13.68
Allotropy	No allotropic transformations of beryllia are known
Electrical resistivity, ohm-cm	
Sintered beryllia of density 2.25 gm/cm ³	
1000°C	80,000,000
1200°C	4,000,000
1400°C	250,000
1600°C	35,000
1800°C	6,500
2000°C	1,800
Mean coefficient of linear thermal expansion, per °C	
25–100°C	$(5.5 \pm 1.0) \times 10^{-6}$
25–300°C	$(8.0 \pm 0.6) \times 10^{-6}$
25–600°C	$(9.6 \pm 0.8) \times 10^{-6}$
25–800°C	$(10.3 \pm 0.9) \times 10^{-6}$
25–1000°C	$(10.8 \pm 1.0) \times 10^{-6}$

*Gm/cm³ × 62.43 = lb/cu ft

†See Fig. 1.3.1 for the thermal conductivities of beryllia bodies of different densities.

‡Cal/(mole)(°C) × 1 = Btu/(lb-mole)(°F)

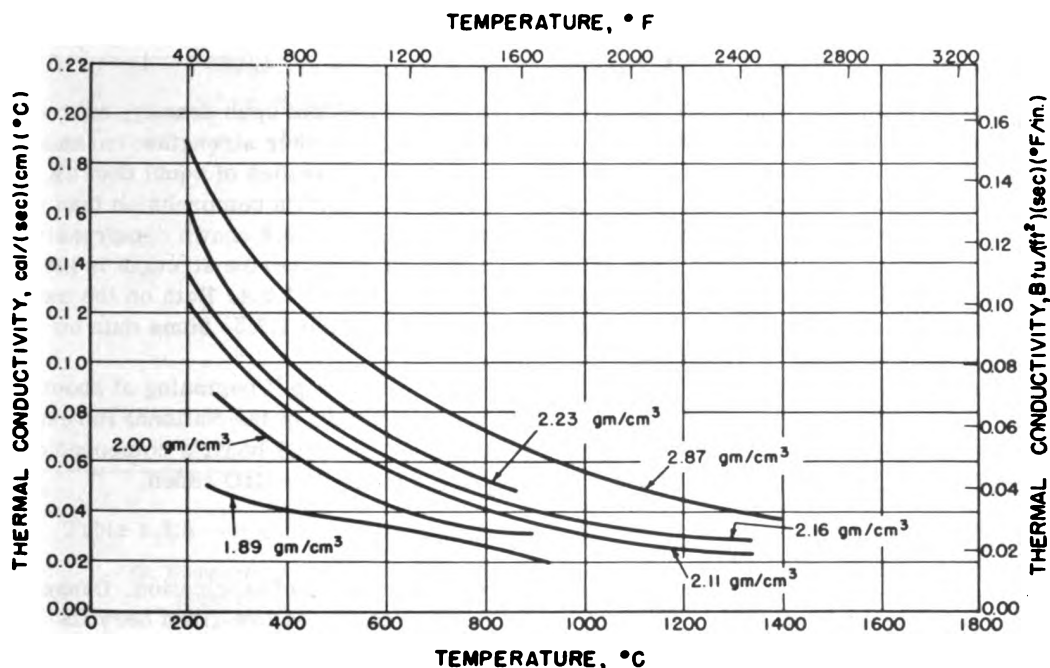


Fig. 1.3.1—Thermal Conductivities of Beryllia Bodies of Different Densities.
 Reprinted from M. C. Udy and F. W. Boulger, *The Properties of Beryllium Oxide*,
 Battelle Memorial Institute, BMI-T-18, Dec. 15, 1949.

close-packed array of oxygen atoms with beryllium atoms in the interstices, also close packed.

LATTICE CONSTANTS

	Room Temperature	1025°C
a_0	2.69 Å	2.72 Å
c_0	4.39 Å	4.43 Å
c_0/a_0	1.63	1.63

REFRACTIVE INDICES

$$\alpha D = 1.719$$

$$\beta D = 1.733$$

HEALTH HAZARDS

Beryllium and its compounds are toxic. Contact with the skin and inhalation of dust or fumes should be avoided. Permissible tolerance levels of beryllia dust in the atmosphere and precautions for handling beryllia in a plant or laboratory should be established by competent medical authority and observed rigorously.

MECHANICAL PROPERTIES

TENSILE AND COMPRESSIVE STRENGTH

The tensile and compressive strengths of beryllia are dependent upon density, method of fabrication, and, of course, temperature. Denser bodies have higher strengths; ceramically extruded bodies are stronger than dust-pressed or slip-cast bodies of equal density. Like most ceramic materials, beryllia is several times stronger in compression than in tension. Tables 1.3.2 and 1.3.3 show tensile strength and Table 1.3.4 shows compressive strength at various temperatures. The effect of density on compressive strength is given in Fig. 1.3.2, and on modulus of elasticity in Fig. 1.3.3 and Table 1.3.4. Data on the modulus of rupture of beryllia at room temperature are given in Table 1.3.5. Some data on shear modulus are given in Table 1.3.6.

Beryllia exhibits the phenomenon of pyroplastic flow, or "creep," beginning at about 1700°F. Creep curves for pure beryllia and for a body developed at the National Bureau of Standards are given in Figs. 1.3.4 and 1.3.5, respectively. The NBS body is composed of 48 moles of BeO, 1 mole of Al_2O_3 , 1 mole of ZrO_2 , and 2 percent of CaO added.

HARDNESS

The hardness of beryllia bodies varies greatly with the method of fabrication. Dense, pure beryllia is rated 9 on Moh's scale of hardness, whereas some low-fired beryllia bodies are as soft as chalk.

THERMAL FRACTURE

The thermal-fracture resistance of beryllia shapes is better than that of most oxide-type ceramic materials. The high thermal conductivity of the beryllia crystal is advantageous in resistance to thermal fracture. Porous beryllia shapes have exhibited a tendency to creep at temperatures above 1900°F. By proper design, this creep can be used to prevent thermal fracture under steady-state conditions, since the creep relaxes stresses before fracture occurs. This creep might be coincident with a loss of strength.

Fracture is obtained in testing cylindrical tubes with a radius ratio of 1.63 (ID 1.00 in.), but when the radius ratio is 1.50, thermal stresses are apparently relaxed by pyroplastic flow before the fracture stress is reached. Fracture can be effected in the latter case, however, with transient heat flow, presumably because the time is insufficient to permit stress relaxation by pyroplastic flow.

Additions of 0.5 percent of alumina or 0.5 or 1.5 percent of an equimolar alumina-zirconia mixture, milled in, increase the thermal-fracture resistance of porous beryllia bodies. The most effective addition is 0.5 percent of the alumina-zirconia mixture which increases the resistance to thermal fracture over that of pure beryllia by a factor of 1.65.

FORMING AND FABRICATION

Beryllia structures are fabricated by five methods: (1) hot pressing, (2) cold or dust pressing, (3) ramming, (4) ceramic extrusion, and (5) slip casting. In each case, beryllia powder is the starting material, and, except for hot pressing, each of the forming operations is followed by a sintering treatment.

In hot pressing, a low-fired, high-purity powder is placed in a suitable die, and pressure is applied while the die is hot. Usually the die is made of graphite and is heated by resistance to 1600° to 2100°C. A pressure of 1000 to 2000 lb/sq in. is applied. Hot-pressed beryllia needs no sintering treatment, since it is formed at high temperature.

Dust pressing, ramming, extrusion, and slip casting are conventional ceramic-forming methods. Generally, water and a small amount of bonding material are added to provide

Table 1.3.2—Tensile Strength of Dense Sintered Beryllia

[E. Ryschkewitsch, Ueber die Zerreisfestigkeit einiger
keramischer Werkstoffe auf der Einstoff-Basis,
Ber. deut. keram. Ges., 22: (1941)]

Temperature, °F	Tensile Strength, lb/sq in.
68	Not determined
930	11,100
1650	6,970
2080	2,060
2370	640

Table 1.3.3—Some Mechanical Properties of Beryllia of Density 2.7 to 2.8 Gm/cm³

(B. Schwartz, Beryllia, Its Physical Properties at Elevated Temperatures,
Massachusetts Institute of Technology, MIT-1083, Feb. 27, 1952)

Temperature, °F	Tensile Strength,* lb/sq in.	Modulus of Elasticity, 10 ⁶ lb/sq in.	Modulus of Rigidity, 10 ⁶ lb/sq in.	Poisson's Ratio
77	15,000	39	14.5	0.34
750	15,000	39	14.5	.34
1470	13,500	39	14.5	.34
1830	10,500	38	14	.35
2010	8,000	28	7	
2190	4,000	10		

*From modulus-of-rupture data

Table 1.3.4—Compressive Strength of Dense Sintered Beryllia

[E. Ryschkewitsch, Ueber die Druckfestigkeit einiger
keramischer Werkstoffe auf der Einstoff-Basis,
Ber. deut. keram. Ges., 22: (1941)]

Temperature, °F	Compressive Strength, lb/sq in.
68	114,000
930	71,000
1470	64,000
1830	36,000
2190	28,000
2250	24,000
2730	17,000
2910	7,100

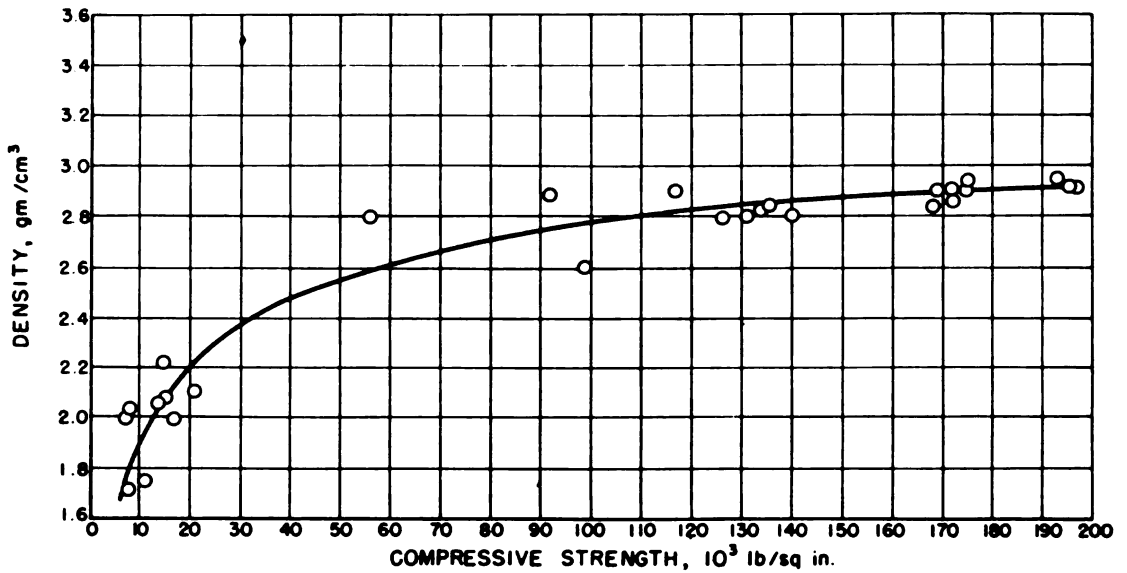


Fig. 1.3.2 — Effect of Density on the Room-temperature Compressive Strength of Beryllia. Reprinted from M. C. Udy and F. W. Boulger, *The Properties of Beryllium Oxide*, Battelle Memorial Institute, BMI-T-18, Dec. 15, 1949.

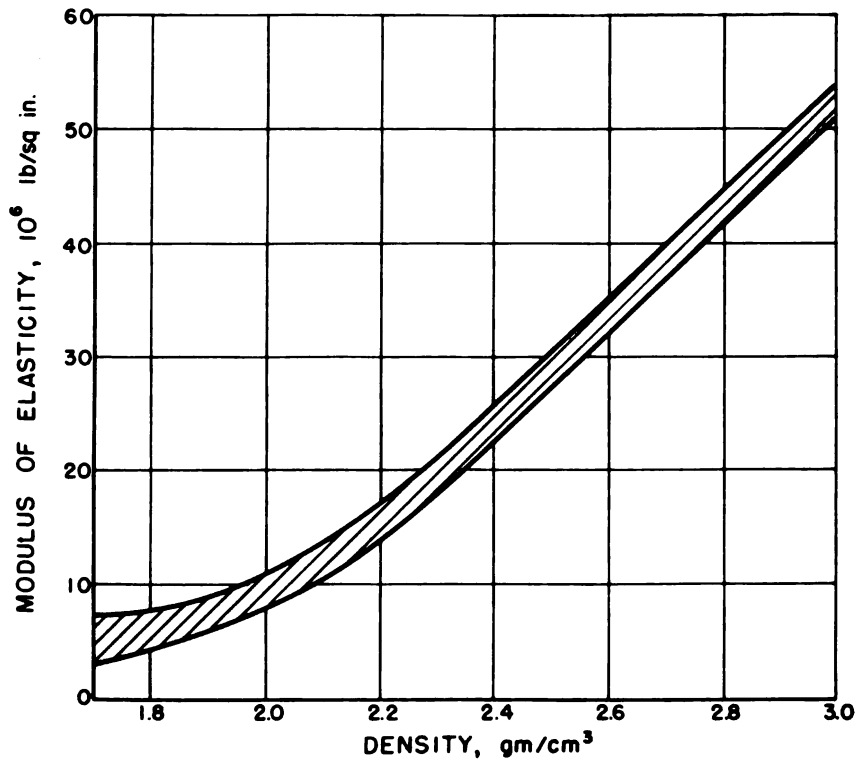


Fig. 1.3.3 — Variation of Modulus of Elasticity of Beryllia with Density. Reprinted from M. C. Udy and F. W. Boulger, *The Properties of Beryllium Oxide*, Battelle Memorial Institute, BMI-T-18, Dec. 15, 1949.

Table 1.3.5 — Room-temperature Modulus-of-rupture Data for Beryllia

Forming Method	Original Mesh Size of Beryllia	Sintering Treatment		Bulk Density, gm/cm ³	Modulus of Rupture, lb/sq in.	
		Temperature, °F	Time at Temperature, hr		2-in. span	3-in. span
Extruded	Minus 200	2800	2	1.98	2,100	
Extruded	Minus 200	3100	3	1.96	2,600	
Extruded	Minus 325	2800	2	1.97	4,800	
Extruded	Minus 325	3100	3	2.03	5,800	
Extruded	Air-classified*	2800	2	2.24	12,500	
Extruded	Air-classified*	3100	3	2.38	14,600	
Dust-pressed	Minus 200	2800	2	1.98		600
Dust-pressed	Minus 200	3100	3	2.01		1400
Dust-pressed	Minus 325	2800	2	2.02		2600
Dust-pressed	Minus 325	3100	3	2.07		4600
Dust-pressed	Air-classified*	2800	2	2.08		7300
Dust-pressed	Air-classified*	3100	3	2.32		8900

*Average grain size was about 7

Table 1.3.6 — Shear Modulus of Beryllia at Room Temperature

(Shear Modulus of Some Pure Oxide Ceramic Materials,
Wright Field Progress Report No. IRE-58, Apr. 19, 1946)

Length, cm	Radius, cm	Twist, °/kg	Shear Modulus, kg/cm ²
14.55	0.0663	60.2	1.04×10^6
17.40	.0730	53.1	0.97×10^6

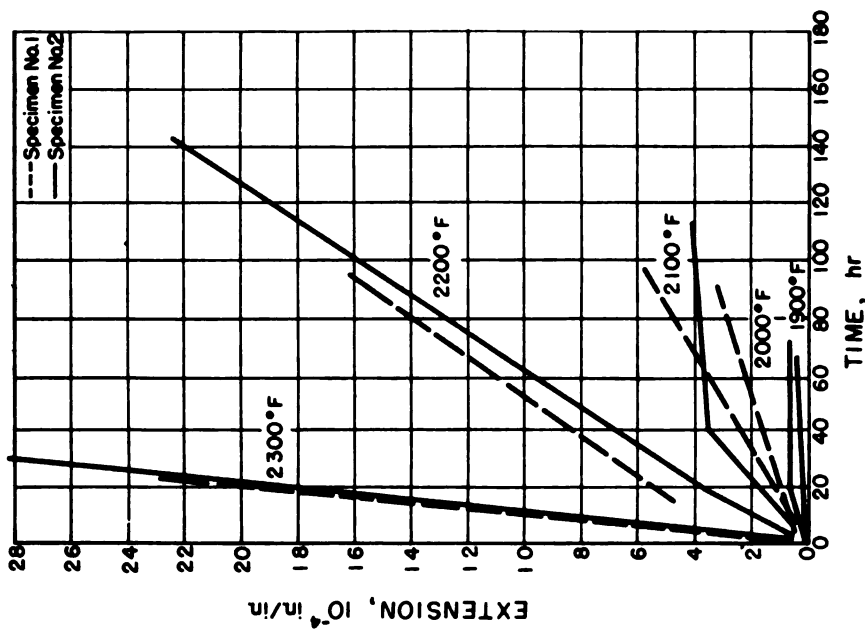


Fig. 1.3.4—Creep Test on Beryllia at 95 lb/sq in. and Indicated Temperature. Reprinted from Fifteenth and Sixteenth Progress Reports on Development of Apparatus and Methods for Measurement of Creep at Temperatures to 3500°F, Engineering Research Institute, University of Michigan, NEPA-1186-MIC-15 and NEPA-1219-MIC-16, October and November 1949.

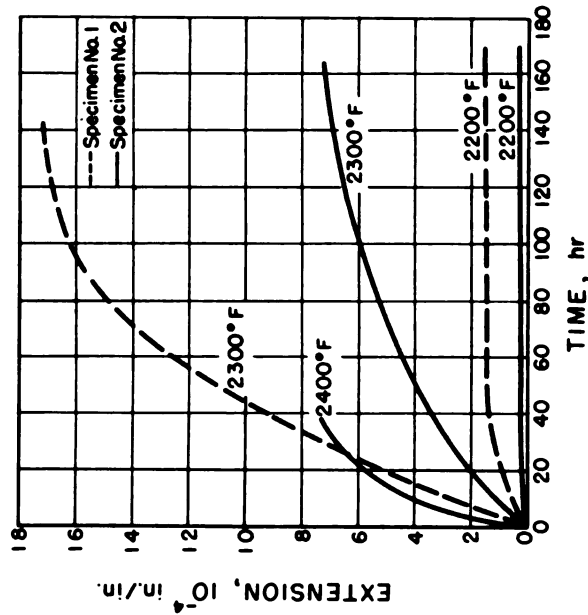


Fig. 1.3.5—Creep Test of National Bureau of Standards Body at 95 lb/sq in. and Indicated Temperature. Reprinted from Twenty-first Progress Report on Development of Apparatus and Methods for Measurement of Creep at Temperatures to 3500°F, Engineering Research Institute, University of Michigan, NEPA-1389-MIC-21, Apr. 20, 1950.

plasticity during forming and strength for the formed structure until sintering. Paraffin, gum, starch, and various similar "binders" are satisfactory and, owing to their organic nature, completely burn out on sintering in an oxidizing atmosphere. Typical satisfactory binders are given in Table 1.3.7. Water is added in various quantities depending on the method of forming: in the case of slip casting, sufficient water to give a slurry that can be poured; a lesser amount, to provide the plasticity necessary for extrusion; or, for dust pressing or ramming, just enough to dampen the powder. When dust-pressed bodies are bonded with paraffin, no water is needed.

Table 1.3.7—Typical Binders for Ceramic Forming of Beryllia

Forming Method	Binder, %	Water, %*
Slip casting	0.25 ammonium alginate	70
Extrusion	6 to 10 gelatinized corn starch	20
Dust pressing	3 starch	5
	4 paraffin (dissolve in CCl_4)	None
	10 to 15 thermal-setting resin†	None
Ramming	10 to 15 thermal-setting resin†	None
	None	None (sinter in the graphite mold)

*Amounts are weight percent of dry beryllia

†An alcohol solution of phenol-formaldehyde resin, BV-1600, supplied by the Bakelite Corporation, Bound Brook, N. J.

Slip-cast bodies are often prepared from suspensions of beryllia in dilute HCl. This method of suspension is convenient because a very fine particle size of beryllia in the casting slip, essential for obtaining strong, dense bodies, is achieved by ball milling in iron equipment, and the contaminating iron is removed by acid leaching, washing, and decantation. A slip having an acid pH remains. The pH is adjusted between 3.0 and 3.5 for best casting qualities after the desired purity has been attained. The slip casts fast, about $\frac{1}{8}$ in. in 15 sec in plaster molds. Dried shapes are very fragile and must be handled carefully until sintered. Casting slips may also be prepared using a gelatinous liquid such as a water-ammonium alginate suspension. The alginate is mixed thoroughly with water to give a thin gelatinous liquid, and dry, finely powdered beryllia is suspended in the liquid, yielding a pourable slip. Satisfactory proportions are given in Table 1.3.7. This slip casts slowly, about $\frac{1}{8}$ in. in 1 hr, but dried shapes are stronger than those cast from acid slip and withstand handling better. There is little difference in fired properties.

Beryllia structures formed by ceramic methods are sintered at temperatures in the range 1700° to 2000°C. If high density is desired, a high sintering temperature is employed. Porous bodies, capable of receiving impregnations, are sintered at lower temperatures. Beryllia is volatile in the presence of water vapor at these sintering temperatures as shown in Tables 1.3.8 and 1.3.9.

The strength and density of porous, sintered beryllia shapes are increased by "imbuing" with a beryllium salt solution, drying, and resintering to convert the salt to beryllium oxide.

The "milling in" of minor amounts of other oxides, such as Al_2O_3 , ZrO_2 , MgO , CaO , ThO_2 , and SiO_2 , singly and in combinations, also increases the strength and density of sintered beryllia bodies.

Table 1.3.8 — Effect of Temperature on Volatilization of Beryllia in Presence of Water Vapor*

(C. A. Hutchinson, Jr., and J. G. Malm, The Volatilization of BeO in the Presence of H₂O, AECD-2345, October 1947)

Temperature, °C	Beryllia Weight Lost in 2.5 hr, %
1000	0.01
1250	.19
1400	.66
1500	1.58
1550	2.24

*Water vapor at ~1 atm and 0.11 mole/min; beryllia density was 2.38 gm/cm³

Table 1.3.9 — Effect of Time on Volatilization of Beryllia in Presence of Water Vapor*

(C. A. Hutchinson, Jr., and J. G. Malm, The Volatilization of BeO in the Presence of H₂O, AECD-2345, October 1947)

Time, hr	Weight Loss, %
4.13	1.7
6.80	5.6
10.80	10.3
15.05	13.3

*Water vapor at ~1 atm; beryllia heated to 1483° to 1528°C; beryllia density was 2.38 gm/cm³

MACHINING

Water-lubricated diamond wheels are used for sawing sintered beryllia. Sintered beryllia blanks may be ground to desired shapes or dimensions by using an abrasive wheel attachment on the lathe. Low-fired beryllia can be turned on a lathe using a hard-ened or high-speed steel tool and then resintered for greater densification; allowances for shrinkage should be considered. Machining unfired beryllia to the final shape is seldom done because pieces may warp or shrink out of size during the sintering that follows. In all machining operations, tool wear is severe.

Sawing extruded columns of unfired beryllia into desired lengths may be done with a "wet" abrasive wheel. However, since the drying that follows may produce cracking or other imperfections in the piece, dry sawing is preferred. To facilitate dry cutting, it is desirable to "scorch the binder," that is, heat the pieces to be cut to 250° to 300°C to partly decompose the organic binder.

CORROSION BEHAVIOR

There are few quantitative data on the corrosion of beryllia. It is quite stable and inert toward most materials except HF, fused alkalis, and water vapor at high temperature.

The reactivity of beryllia is decreased by higher sintering temperatures. Beryllia does not dissociate appreciably at ordinary temperatures.

Beryllia and water vapor react to form a volatile compound at temperatures above 1250°C. The volatilization rate increases with increasing temperature and is too rapid to be accounted for by the vapor pressure of beryllia (see Tables 1.3.8 and 1.3.9). On cooling, the volatile compound decomposes and condenses as beryllia.

Some data on the attack of beryllia by PbO liquid and vapor are given in Table 1.3.10.

Beryllia reacts slowly with concentrated HCl but more rapidly with the boiling acid. Concentrated nitric acid dissolves beryllia more slowly than does concentrated HCl. Sulfuric acid has but slight effect. Beryllia is dissolved rapidly by HF.

Table 1.3.10 — Resistance of Beryllia Bodies to Attack by Lead Oxide Liquid and Vapor

[R. F. Geller, P. J. Yavorsky, B. L. Steierman, and A. S. Creamer,
Studies of Binary and Ternary Combinations of Magnesia, Calcia, Baria, Beryllia,
Alumina, Thoria, and Zirconia in Relation to Their Use as Porcelains,
J. Research Natl. Bur. Standards, (1946) (Research Paper No. 1703)]

Composition, wt-%	Absorption, %	Treatment for 4 hr at 1100°C	Result
BeO	0.02	Partly immersed	Original 0.5-in. diameter of immersed portion reduced by 0.008 in.
99 BeO, 1 MgO	.02	In vapor	Color change to 1-mm depth; weight loss 1.2%
99 BeO, 1 MgO	.02	Partly immersed	Discernible, but slight attack on immersed portion
99 BeO, 1 CaO	.01	Partly immersed	Only 0.007-in. decrease in diameter, but micro- scope shows interstitial penetration of PbO throughout specimen

Fused alkalis, alkali carbonates, and pyrosulfates dissolve beryllia readily. However, beryllia is fairly resistant to alkali solutions. The degree of reactivity depends on prior treatment.

No reaction occurs with H_2O_2 , hydrogen, nitrogen, CO_2 , SO_2 , sulfur, bromine, iodine, or ammonia and probably not with CO. With fluorine a fluoride is readily formed. There is a slight room-temperature reaction with chlorine which ceases at 140°C and starts again at 600°C. With CCl_4 vapor, an anhydrous chloride is formed. With CS_2 there is no reaction in 3 hr below 700°C but complete conversion in 1 hr at 1325°C.

Beryllia is corroded only slowly by $COCl_2$ at 455°C. By this means it can be purified from iron, aluminum, and calcium which form volatile chlorides at this temperature. Attack is rapid at higher temperatures.

Beryllia reacts at high temperatures with carbon to give Be_2C . With carbon reduction in the presence of a heavy metal, such as copper, metallic beryllium is formed as an alloy of the metal, instead of the carbide.

At high temperatures, silicon will react with beryllia to give the silicide and with boron to give the boride.

Beryllia can be reduced by both titanium and zirconium, although the reaction may not go to completion.

Beryllia is stable toward iron and similar metals, and probably lithium, under neutral or reducing conditions. It is unaltered by NaK at 600°C, but only when very dense and highly vitrified. Otherwise, it is impregnated and sometimes distorted on exposure to NaK.

Magnesium and calcium do not react with beryllia, nor does gallium at 1000°C.

Resistance to erosion, like resistance to chemical attack, increases with higher fired and denser bodies.

PROTECTIVE TECHNIQUES

A coating for beryllia might be useful in a reactor to confine fission fragments or to protect the beryllia from a corrosive coolant. A ceramic coating of the conventional glaze type would probably be unsatisfactory. Besides bringing undesirable atoms into the structure, such a coating would have poor resistance to thermal shock. On the other hand, a metallic coating might be considered; molybdenum may be promising. Sintered beryllia disks have been painted around the cylindrical surface with a water slurry of molybdenum powder. When this assembly was sintered in a high-vacuum atmosphere to densify the molybdenum, the coating was continuous, was free of cracks, and adhered tightly to the beryllia.

Porous beryllia, fabricated by ceramic methods, is receptive to impregnation. The pores in such a structure are interconnected in a way that permits about 99 percent of the pore volume to be filled by liquid during an impregnation treatment.

CONSTITUTIONAL DIAGRAMS

Minor additions of other oxides to beryllia increase the strength and density of beryllia bodies when sintered. Constitutional diagrams of beryllia with various other oxides are readily available in the literature. Typical constitutional diagrams and their sources are noted in Table 1.3.11.

Table 1.3.11 — Sources of Various Constitutional Diagrams of Beryllia and Other Oxides

Diagram	Source
$\left. \begin{array}{l} \text{BeO-ZrO}_2\text{-Al}_2\text{O}_3 \\ \text{BeO-ThO}_2\text{-Al}_2\text{O}_3 \\ \text{BeO-MgO-Al}_2\text{O}_3 \end{array} \right\}$	R. F. Geller, P. J. Yavorsky, B. L. Steierman, and A. S. Creamer, Studies of Binary and Ternary Combinations of Magnesia, Calcia, Baria, Beryllia, Alumina, Thoria, and Zirconia in Relation to Their Use as Porcelains. <i>J. Research Natl. Bur. Standards</i> , 36: 277-312 (1946) (Research Paper No. 1703)
$\left. \begin{array}{l} \text{BeO-CaO-ZrO}_2 \\ \text{BeO-CeO-ZrO}_2 \end{array} \right\}$	O. Ruff, F. Ebert, and W. Loerpabel, Beitrage zur Keramik hochfeuerfester Stoffe. V. Die Ternaren Systeme: $\text{ZrO}_2\text{-ThO}_2\text{-CaO}$, $\text{ZrO}_2\text{-ThO}_2\text{-MgO}$, $\text{ZrO}_2\text{-BeO-CaO}$, $\text{ZrO}_2\text{-BeO-CeO}$, <i>Z. anorg. u. allgem. Chem.</i> , 207: 310-312 (1932).

VOLATILITY OF BERYLLIA

Beryllia is detectably volatile at temperatures as low as 1250°C in the presence of water vapor. Weight lost by beryllia shapes and the rounding of corners during sintering in gas-fired furnaces are attributed to water vapor in the atmosphere arising from combustion of the fuel. In vacuum or inert atmosphere, helium, or mixtures of nitrogen and hydrogen, beryllia may be heated to 2000°C without appreciable loss by volatilization. Fig. 1.3.6 gives the reaction rate of beryllia with steam at 1400°C.

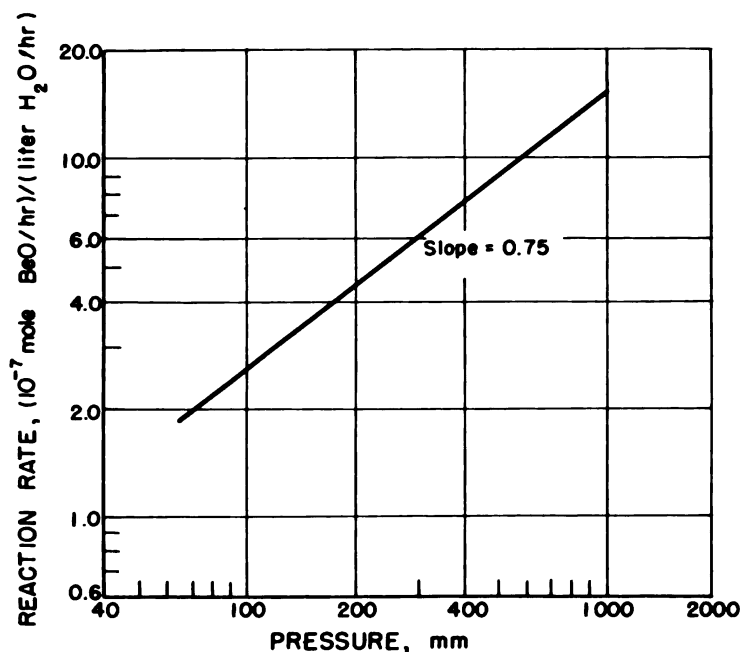


Fig. 1.3.6—Effect of Pressure on the Rate of Reaction of Beryllia with Steam at 1400°C. Reprinted from L. Grossweiner, Reaction of Beryllia with Steam, pp 79–81 in Summary Report for January, February, and March, 1950; Chemistry Division, Section C-II, Argonne National Laboratory, ANL-4449, Oct. 19, 1950.

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CHAPTER 1.4

Beryllium and Its Alloys

J. T. Stacy

REACTOR APPLICATION

Beryllium with its low thermal-neutron-absorption cross section and high neutron-scatter cross section is an excellent moderator and reflector for reactors. Furthermore, the neutron multiplication may be increased by a small increment through beryllium (γ, n) and ($n, 2n$) reactions. Beryllium also has the added advantages of being light in weight, having a relatively high thermal conductivity, and having a high melting point. Consideration of its use as a component material in fuel elements has been based on these favorable properties. However, these useful qualities of beryllium are somewhat countered by its low ductility, difficulty of fabrication, generally poor corrosion resistance to water and the various cooling media of proposed reactor designs, and its high cost.

Occasional mention of beryllium test pieces possessing fairly good ductility or showing good corrosion resistance in water has seemingly indicated that some of the poorer properties ascribed to beryllium might result from impurities in the metal, although variations in the test procedures and fabrication may in fact be responsible for the deviations. No crystallographic basis for beryllium's lack of ductility appears to exist, although its small atomic volume would lead one to expect that beryllium would be harder than other hexagonal metals.

Considerable effort has been made in recent years to improve the purity and properties of commercial beryllium, and progress has been made in fabricating the metal by powder-metallurgy methods and by both hot- and warm-extrusion processes.

ABUNDANCE AND AVAILABILITY

The abundance of beryllium in the earth's crust is estimated at 0.0004 to 0.001 percent. Although there are approximately 30 beryllium-containing minerals, only one is of commercial importance. This is beryl, a beryllium-aluminum-silicate ($3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Three other potential mineral sources of beryllium are chrysoberyl, phenacite, and helvite.

Beryl occurs as widely scattered crystals in certain pegmatites, whose beryl content averages less than 1 percent. It is produced generally as a by-product of other mining operations (mica, feldspar, and lithium) by hand sorting, which probably limits the recovery to about 25 percent. Brazil, Argentina, and India lead the world in the production of beryl. Domestic beryl comes chiefly from South Dakota, although Colorado, Maine, New Hampshire, Connecticut, and Massachusetts produce limited quantities.

The beryllia content of beryl varies from 8 to 14 percent, which is equivalent to a beryllium content of 3 to 5 percent. About 75 percent of the beryllia is recovered during processing.

The known domestic beryl reserves amount to between 12,000 and 16,000 short tons. In 1944, the year of peak production, 388 tons of beryl were shipped from United States mines. The estimated potential of world production is 3700 tons/year.

The cost of beryllium varies from \$50 to \$200/lb depending on the form desired, with fabricated billets varying between \$90 and \$125/lb.

EXTRACTION AND PURIFICATION

Beryllium products are made from beryl ore by three companies in the United States:

Beryllium Corporation, Reading, Pennsylvania
Brush Beryllium Corporation, Cleveland, Ohio
Clifton Products, Inc., Painesville, Ohio

Of these three companies, the Brush Beryllium Company has been the major producer of metallic beryllium, although considerable electrolytic flake beryllium has been produced by Clifton Products, Inc.

The most important domestic process for producing metallic beryllium, i.e., the Brush process, the magnesium-reduction process, or the Sawyer-Kjellgren process, is outlined in Fig. 1.4.1. The beryl ore is usually arc-furnace melted and quenched in water before acid treatment to increase the reactivity. During processing, silicon is removed as an insoluble silicic acid and aluminum as an alum, formed by treating with ammonium sulfate. A high-purity beryllium oxide is obtained by roasting the beryllium sulfate at 2370°F. Preparation of the metal is carried out in a graphite-lined furnace at about 1650°F by magnesium reduction of the fluoride; calcium is equally good for reduction but is more expensive. After the reaction is completed, the temperature is raised to 2370°F, and molten beryllium floats to the top where it is allowed to solidify. The excess beryllium fluoride forms a slag containing some beryllia. This is leached with ammonium fluoride, and the recovered beryllium content is returned to cycle.

The terms "pebble" and "flake" beryllium are sometimes used. These refer to the manufacturing method; i.e., pebble beryllium is produced by the magnesium reduction of BeF_2 , while flake beryllium is produced by the electrolysis of fused salts containing BeCl_2 .

Figure 1.4.1 shows several methods of treating the raw beryllium pebble involving re-melting with purifiers, vacuum casting, extrusion, and powder preparation. The powder techniques are known as "Q-process" beryllium, and since July 1950, the standard Brush powder process has been QMV beryllium. The products of other processes are denoted as QT, QPT, QM, and QRM. These are noted in the figure (see also Powder Metallurgy). The QMV specification for warm- or hot-pressed beryllium (Brush BP-QMV) are:

Be	> 98.00% (assay)	Mg	< 0.30%
BeO	< 1.50%	Al	< 0.15%
Be ₂ C	< 0.35%	N ₂	None
Fe	< 0.20%		

The analytical differences among various grades of beryllium are shown in Table 1.4.1.

Other methods for producing the oxide and the metal include the Joy-Windecker, the Copauk-Kawecki, the DEGUSSA, and the electrolytic processes.

The Joy-Windecker process consists of fusing the beryl with Na_2CO_3 and treating with H_2SO_4 . This is followed by removing much of the aluminum sulfate by precipitating it with $(\text{NH}_4)_2\text{SO}_4$ and subsequently precipitating most of the iron, some remaining aluminum, and some beryllium as hydroxides with Na_2CO_3 . After filtering, the filtrate is reprecipitated

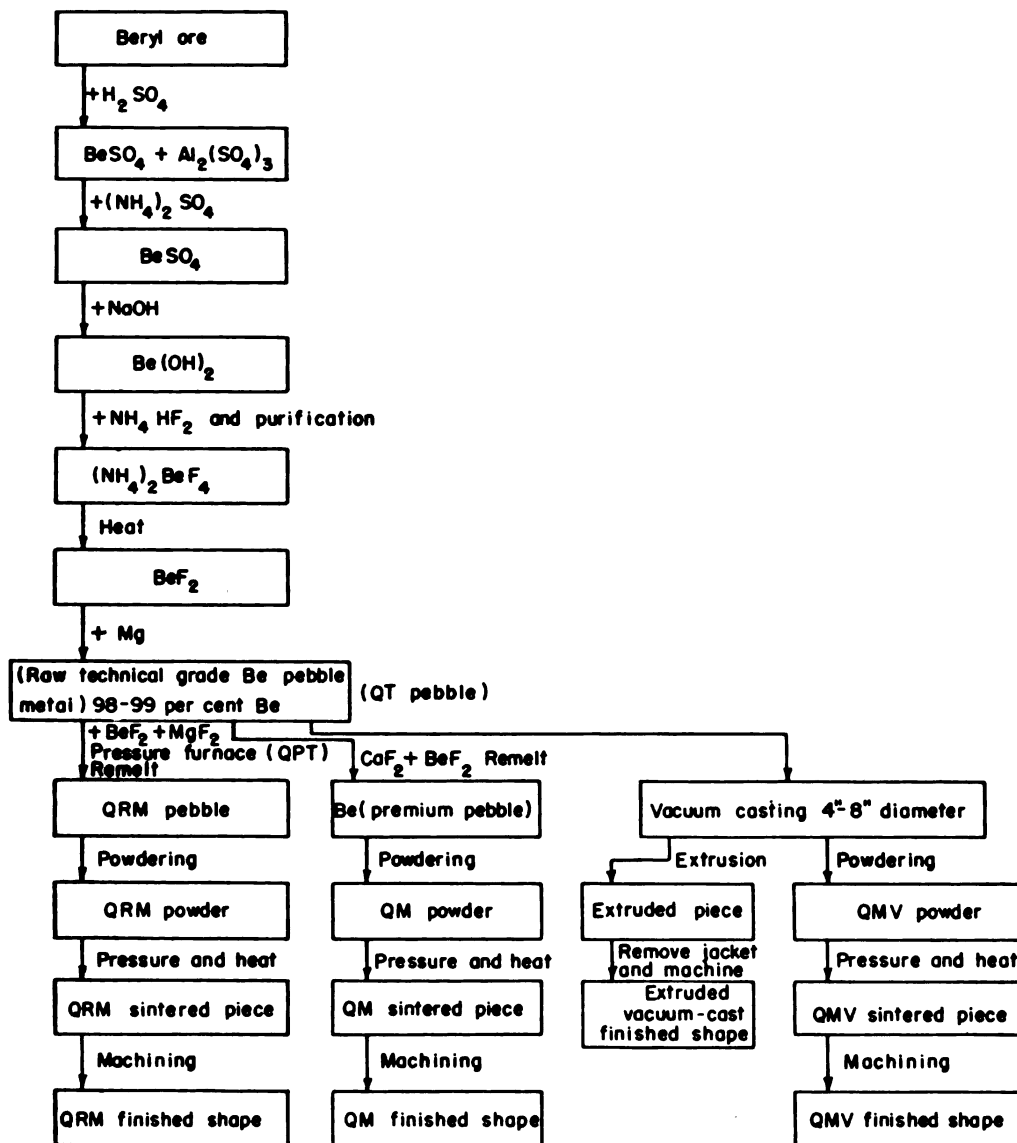


Fig. 1.4.1 — Flowsheet of the Production Processing of Beryllium. Reprinted from *Beryllium and Beryllium Oxide Production and Development*, November 21, 1949, Special Materials Division, New York Operations Office of the AEC, NYO-110, June 9, 1950.

with Na_2CO_3 , and the crude hydroxide is redissolved in H_2SO_4 . Adjusting the pH with ammonia precipitates the remaining iron and aluminum which are filtered off, and the beryllium is then precipitated with ammonia and ignited to beryllia.

In the Copauk-Kawecki process, the beryl ore is powdered and mixed with Na_3FeF_6 and sintered at 1380°F . After the product has been leached with water (containing a small amount of potassium permanganate) and filtered, $\text{Be}(\text{OH})_2$ is precipitated from the filtrate with NaOH and ignited to beryllia. The beryllia is suitable for alloy and metal production, but because it contains some NaF , it is not suitable for refractory use.

Table 1.4.1 — Major Analytical Differences Among Various Grades of Beryllium
(Beryllium and Beryllium Oxide Production and Development, NYO-110, June 9, 1950)

BERYLLIUM-METAL PLATES OR PEBBLES						
Grade	Primary (or technical)			Remelted in CaF ₂ -BeF ₂ flux-premium	Remelted in MgF ₂ -BeF ₂ slag in pressure furnace	Vacuum melted
Form	Plates	Pebbles		Plates	Pebbles	Billets
BeF ₂ reduced to Be, %	70	70	55
Assay	96-99	96-99	99+	99+	99+	99+
BeO	0.1-0.25	0.1-0.25	0.1-0.25	0.1-0.25	0.1-0.25	0.1-0.25
Mg	0.5-1.0	0.5-0.8	0.15-0.40	0.05-0.09	0.05-0.25	0.01-0.05
Ca	0.001-0.005	0.001-0.005	0.001-0.005	0.1-0.2	0.001-0.005	0.001-0.005
Be ₂ C	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3

POWDER-SINTERED SHAPES					
Grade	QT	QPT	QM	QRM	QMV
Source of Be metal	Open- furnace primary	Pressure- furnace primary	Remelted under CaF ₂ -BeF ₂ flux open furnace	Remelted under MgF ₂ -BeF ₂ slag in pressure furnace	Vacuum cast, powdered
Assay	98.0+	98.5+	98.5+	98.7+	98.7+
BeO	1.0-1.8	1.0-1.8	1.0-1.8	1.0-1.8	1.0-1.8
Mg	0.35-0.60	0.15-0.35	0.05-0.09	0.05-0.25	0.01-0.05
Ca	0.001-0.005	0.001-0.005	0.1-0.2	0.001-0.005	0.001-0.005
Be ₂ C	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3
Density	1.84-1.86	1.85-1.86	1.85-1.86	1.85-1.86	1.85-1.86

The DEGUSSA process consists of sintering the beryl ore at 2730°F with CaO in excess of the amount required to form CaO·Al₂O₃ and CaO·2SiO₂ and treating this product with H₂SO₄. SiO₂ and CaSO₄ are precipitated, and treatment with (NH₄)₂SO₄ precipitates the aluminum. H₂O₂ is used to oxidize the iron which is precipitated with CaCO₃. The beryllium is precipitated by ammonia treatment as a hydroxide which is then ignited to the oxide. A fused mixture of beryllium and sodium chlorides is electrolyzed to secure beryllium metal.

Beryllium chloride for the electrolytic process is formed by passing chlorine over a mixture of the oxide and carbon at about 1830°F. This is electrolyzed in molten NaCl at about 1345°F using a minimum of 5 v and a NaCl-impregnated graphite anode. When the bath reaches 1510°F, the process is stopped. The beryllium is deposited in flake form on the wall of a stainless steel or nickel pot. The BeCl₂ is hygroscopic and must be kept out of contact with air. To form massive metal, these flakes are briquetted and fused in a closed crucible with a flux of 10 percent BeF₂ and 90 percent BaCl₂. In order to produce cheaper beryllium, attempts have been made to chlorinate the beryl ore directly, keeping the impurities low by selective chlorination or condensation, purifying the BeCl₂ by distillation in hydrogen, or purifying the NaCl + BeCl₂ electrolyte by preliminary electrolysis. This latter method appeared to be too costly because of the loss of beryllium during the removal of the aluminum which was present as AlCl₃ in the electrolyte during the preliminary electrolysis.

PHYSICAL AND CHEMICAL CONSTANTS

The physical and chemical constants of beryllium are given in Table 1.4.2.

Table 1.4.2—Physical and Chemical Constants of Beryllium

Thermal-neutron-absorption cross section, barns/atom	0.0090 ± 0.0005
Density,* gm/cm ³	
X-ray (25°C)	1.8477 ± 0.0007
Extruded QMV	1.847
Extruded QM	1.808–1.855
Extruded QT	1.841–1.849
Extruded Premium	1.79–1.86
Melting point, °C	1315
Boiling point, °C	2970
Heat of vaporization (sublimation), cal/gm	
900°–1280°C	8,380 ± 40
Heat of fusion, cal/gm	259
Heat of vaporization, cal/gm	5930
Vapor pressure	
900°–1280°C	$\log P \text{ (atm)} = 6.186 + 1.454 \times 10^{-4} T - \frac{16,700}{T(^{\circ}\text{K})}$
Allotropic transformation	No indication of a transformation from X-ray or cooling-curve data up to 1250°C. At that temperature some indication of a transformation has been observed.
Specific heat,† cal/(gm)(°C)	
–200°C	0.02
–100°C	.20
0°C	.42
100°C	.51
200°C	.57
400°C	.64
600°C	.69
800°C	.74
Effect of purity on specific heat	
Percent Be	cal/(gm)(°C)
97.5	0.32–0.37
98	.34–.38
98.5	.36–.38
99	.38–.41
99.5	.44–.47
~100	.51–.56
Enthalpy (H _T – H ₀), cal/gm	
100°C	200
200°C	370
300°C	520
400°C	670
500°C	800
600°C	930
Entropy, cal/(mole)(°C)	
25°C, solid Be	2.28 ± 0.02
25°C, vapor Be	32.55 ± 0.01
Electrical conductivity, percent IACS‡	
QMV Beryllium, hot pressed	38.1
QMV Beryllium, extruded	42.3
QRM Beryllium, extruded	37.3–38.7
QRM Beryllium	34.5
Beryllium may be superconducting below –263°C	

Table 1.4.2 — (Continued)

Thermal-expansion coefficient, per $^{\circ}\text{C} \times 10^6$

Temperature range, $^{\circ}\text{C}$	Direct measurement (99.28% extruded Be)	X-ray (97% Be + 2% O)
25–100	11.54	11.6
25–300	14.44	14.5
25–500	15.95	15.9
25–700	17.23	17.0
25–900	...	17.9
25–1000	18.77	18.4

Thermal conductivity, $\frac{1}{2}$ cal/(sec)(cm)($^{\circ}\text{C}$)

Temperature, $^{\circ}\text{C}$	Vacuum cast, extruded	Flake, extruded	QM
0	0.361	0.355†	0.40†
100	.34†	.33†	.385
200	.32	.305	.375
300	.30	.28	.36
400	.28	.26	...
500	.26	.235	...
600	.24	.21	...

*Gm/cm³ $\times 62.43$ = lb/cu ft†Cal/(gm)($^{\circ}\text{C}$) $\times 1.0$ = Btu/(lb)($^{\circ}\text{F}$)

‡International Annealed Copper Standard

§Cal/(sec)(cm)($^{\circ}\text{C}$) $\times (2.419 \times 10^3)$ = Btu/(hr)(ft)($^{\circ}\text{F}$)

¶Extrapolated

CRYSTALLOGRAPHY

STRUCTURE

Beryllium has a close-packed hexagonal structure with an abnormally low c/a ratio.

LATTICE CONSTANTS

The following lattice constants have been determined: $a_0 = 2.2858$ Å, $c_0 = 3.5842$ Å, and $c_0/a_0 = 1.5680$. The effect of temperature on the lattice constants is shown in Fig. 1.4.2. The interatomic distances have been reported as $d_1 = 2.225$ and $d_2 = 2.286$ Å at room temperature. For a coordination number of 12, the atomic radius has been calculated to 1.123 Å for beryllium.

The unit cell contains two atoms and has a volume of 16.1×10^{-24} cm³.

PREFERRED ORIENTATION

Preferred orientation is induced in beryllium by extrusion. X-ray analysis has shown that the 0001 (basal) planes and a $10\bar{1}0$ direction are lined up almost parallel to the extrusion axis. Consequently, the basal planes are also roughly parallel to the fiber axis. Beryllium rods extruded with reduction ratios of 500 to 1 and 16 to 1 showed this type of preferred orientation. When the latter rod was annealed at 1830°F, all but small traces of the preferred orientation were removed. The angular spread of the fiber axis for the rod extruded with a 500-to-1 reduction was measured to be about 12° to 15°, which roughly represented the perfection of preferred orientation.

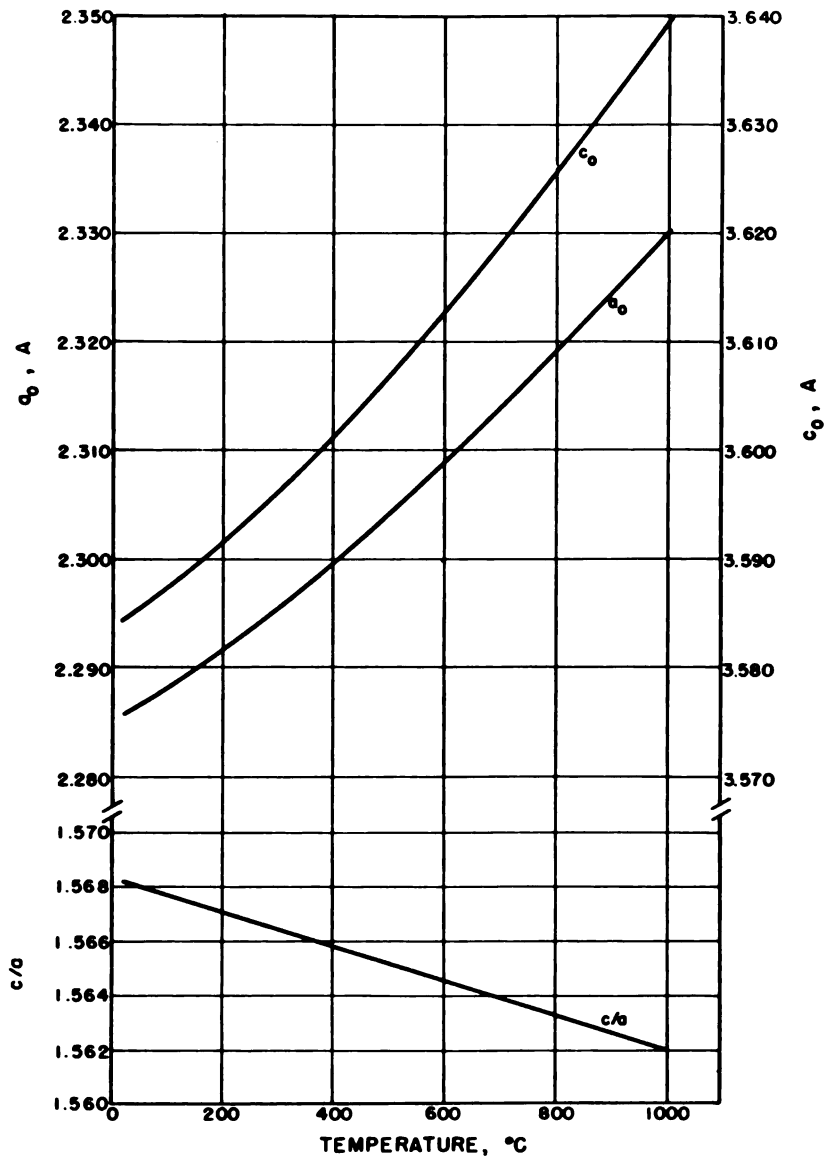


Fig. 1.4.2 — The Effect of Temperature on the Lattice Constants of Beryllium. Based on data in P. Gordon, Some Measurements of the Thermal Coefficients of Expansion of Beryllium, AECD-2426, Oct. 1948.

SLIP PLANES

Slip in beryllium crystals at room temperature takes place on the 0001 planes in a $\bar{2}\bar{1}\bar{1}0$ direction.

HEALTH HAZARD

Beryllium and its compounds are toxic. Permissible tolerance levels of fumes and dust in the atmosphere and precautions for handling beryllium and its compounds should be established by consultation with competent industrial medical authorities.

HANDLING AND STORAGE

Safety precautions should be observed at all times during the handling of beryllium because of the health hazard. Massive beryllium presents no problem in storage, but beryllium powder tends to increase in oxygen content with time and should be kept stored away from air and moisture.

MECHANICAL PROPERTIES

The mechanical properties of beryllium are quite dependent on the degree of anisotropy and the purity of the metal. Extruded beryllium is anisotropic. The gross longitudinal grain fibering in extruded beryllium can be eliminated by annealing at temperatures above 1380°F, while the preferred orientation of extruded beryllium persists to some extent even after annealing at 1830°F. However, no evidence of anisotropy is observed in the mechanical properties of beryllium which has been produced by hot pressing the powder. Generally, an increase in the purity of beryllium appears to result in an increase in the tensile properties. Tests on sintered beryllium have shown that increasing amounts of magnesium adversely affect the tensile strength and elongation values.

Ordinarily, beryllium is a metal of fairly high tensile strength, high modulus of elasticity, low Poisson's ratio, and low ductility. There appears to be no fundamental crystallographic reason for the poor ductility of beryllium. Its similarity in structure to titanium and zirconium lead one to expect beryllium to be ductile in the pure state. However, despite considerable effort to increase the purity of beryllium, the available metal remains quite brittle.

The results of mechanical tests on beryllium may be affected by damage to the specimen surfaces during machining. Even the most careful machine work appears to cause surface damage in some instances to this brittle material. Annealing at 1470°F has been found to eliminate the effects of surface damage in the case of cast and extruded beryllium. However, there appears to be evidence that, for accurate test results, cold-worked and heat-treated or hot-worked beryllium must be chemically or electrolytically polished prior to testing. Lapping, electrolytic polishing, or mechanical polishing is satisfactory for the hot-pressed metal. In this latter case, it should be noted that grinding has been reported to cause more surface damage to hot-pressed beryllium than careful machining.

The following chemical and electrolytic etchants have been used to remove the surface layer of beryllium to a depth of 0.003 to 0.006 in. or more prior to mechanical testing:

Electrolytic: 15 min at about 2.5 amp in a solution of 3 parts methyl alcohol, 1 part 10% HNO₃, and 1 part 2.5% NaF.

Chemical: 5 to 10 min up to 220°F (removes about 0.001 in./min) in a solution of 7% Cr₂O₃, 85% H₃PO₄, 5% H₂SO₄, and water. For slower attack, a temperature of 110°F has been recommended.

In collecting the tensile and compression data from the literature, it has not always been possible to determine whether the specimens were etched prior to testing. Where definite information was given, it is so reported in the following sections; otherwise, it is likely that the specimens were not etched. This appears to be particularly true of the earlier data.

Beryllium is sensitive to the rate of strain and to the size and type of mechanical test bar.

TENSILE PROPERTIES

Tables 1.4.3 and 1.4.4 present room-temperature tensile data for various types of beryllium. Figure 1.4.3 also illustrates the marked differences between transverse and longitudinal properties in extruded beryllium. Stress-strain curves for sintered beryllium and extruded beryllium are given in Fig. 1.4.3.

The effects of extrusion reduction, extrusion temperature, and annealing temperature on the tensile properties of extruded beryllium are shown in Table 1.4.5 and Figs. 1.4.4, 1.4.5, and 1.4.6. Table 1.4.5 is concerned only with low-temperature extrusion, i.e., about 800°F as carried out in the Brush "Extru-Powder" process, while the figures deal with hot extrusion at temperatures above 1200°F, generally about 1800° to 1900°F.

The elevated-temperature tensile properties of extruded beryllium as determined by short-time high-temperature tensile tests are given in Fig. 1.4.7. The tensile properties at 1000°F are given for various types of beryllium in Table 1.4.6.

As shown in Fig. 1.4.7, the change in ductility at about 1110°F is believed related to the change in the mechanism of fracture from the intragranular to intergranular type.

The effects of the strain rate on the room-temperature tensile properties of pressed and sintered beryllium powder are given in Table 1.4.7. Figure 1.4.8 shows the effects of strain rate on the elevated-temperature tensile properties of extruded beryllium.

COMPRESSIVE PROPERTIES

The fracture strength in compression of a single crystal of beryllium has been reported as 285,000 lb/sq in.

Table 1.4.3 — Tensile Strength and Elongation of Extruded Flake, Cast, and Powder Beryllium

(BBC-48, June 1951, based on MIT test results)

Material	Ultimate tensile strength, lb/sq in.	Elongation, %
Flake, as extruded		
Longitudinal	46,600	0.55
Transverse	29,100	.30
Flake, extruded and annealed 1 hr 1470°F		
Longitudinal	63,600	5.0
Transverse	25,500	0.3
Cast, as extruded		
Longitudinal	32,700	0.36
Transverse	19,400	.30
Cast, extruded and annealed 1 hr at 1470°F		
Longitudinal	39,900	1.82
Transverse	25,500	0.18
Vacuum cast and extruded at 1290°F		
As extruded	60,300	0.30
Extruded and etched	59,800	.31
Extruded and annealed 1 hr at 1470°F	47,600	2.74
Extruded at 1900°F (33:1 extrusion ratio)		
20- to 28-μ powder	106,350	12.1
28- to 40-μ powder	102,600	15.3

Table 1.4.4 — Properties of Hot-pressed and Extruded Beryllium*

(Report BBC-48, June 1951, based on MIT and Brush results)

Material	Average ultimate strength, lb/sq in.	Average elongation, %	Average yield strength, lb/sq in.	Remarks
QM, remelted in CaF_2 and BeF_2	70,000	7.9	26,800	Hot extruded-MIT
QT	73,300	8.4	30,000	Hot extruded-MIT
QMV	94,500	10.3	44,000	Hot extruded-MIT
QMV	109,400	2.0	...	Warm extruded-Brush†
QMV	97,000	5.7	...	Warm extruded-Brush, plus 20 min at 1380°F

*Specimens etched prior to testing to remove possible surface damage

†Extruded between 750° and 840°F

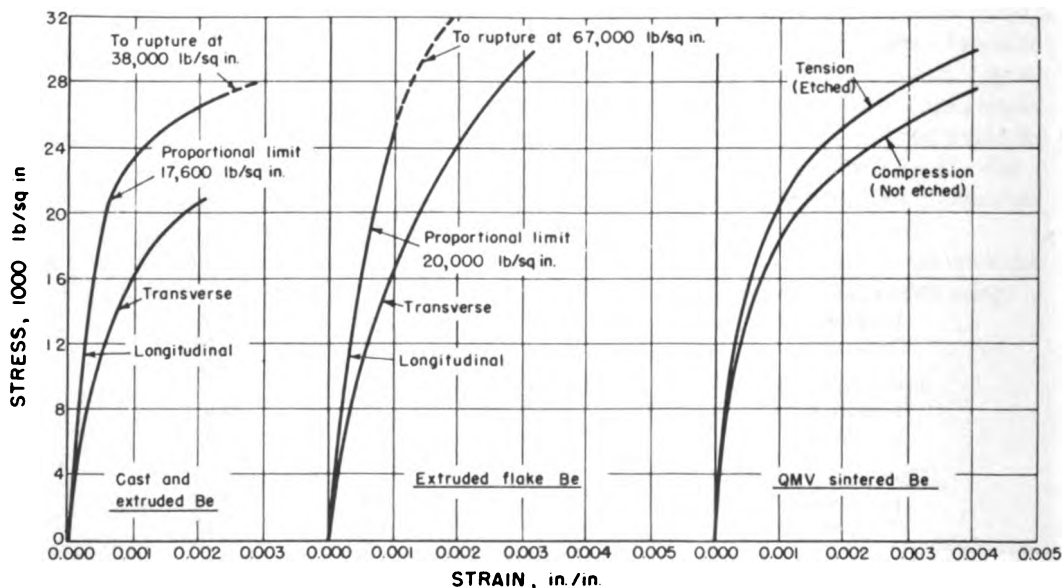


Fig. 1.4.3 — Typical Stress-strain Curves for Sintered Beryllium and Extruded Beryllium. Compiled from data of Lillie, Gordon, and Kaufmann, *The Mechanical Properties of Beryllium*, J. Met. and Cer., No. 1, July, 1948, and W. W. Beaver and B. C. Raynes, *Mechanical Properties of Beryllium Metal*, I. Hot-Pressed Powder, BBC-48, June 26, 1951. (Specimen history unknown except where indicated.)

**Table 1.4.5 — Mechanical Properties of Sintered QRM
Beryllium Extruded at 800°F**
(Brush "Extru-Powder" Process, from NYO-110)

Extrusion ratio	Condition	Ultimate strength, lb/sq in.	Proportional limit, lb/sq in.	Elongation, % in 4 × D
11	As extruded	108,000	...	0.5
	Electrolytically polished	107,000	...	1.0
	Annealed	76,000	...	5.5
	Annealed and electro- lytically polished	79,000	...	4.0
7.7	As extruded*	96,000	72,000	0.5
	Electrolytically polished*	100,000	70,000	...
	Annealed*	79,000	24,000	2.5
	Annealed and electro- lytically polished	73,000	41,000	2.6
4.7	As extruded*	89,000	80,000	1.5
	Electrolytically polished*	90,000	75,000	1.5
	Annealed	65,000	20,000	2.0
	Annealed and electro- lytically polished	73,000	37,000	2.9

*Selected values as data were few and erratic. Others are averages of what may be considered valid data

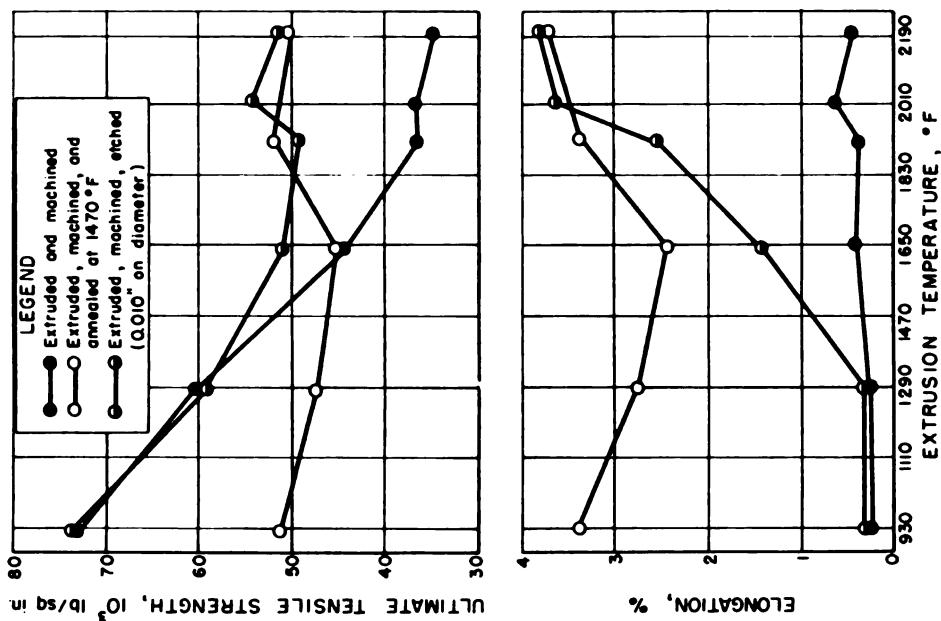


Fig. 1.4.5 — The Effect of Extrusion Temperature on the Tensile Properties of Beryllium. Reprinted from D. W. Lillie, P. Gordon, and A. R. Kaufmann, The Mechanical Properties of Beryllium, J. Met. and Cer., No. 1, July 1948. (Specimens not etched to remove machined surface.)

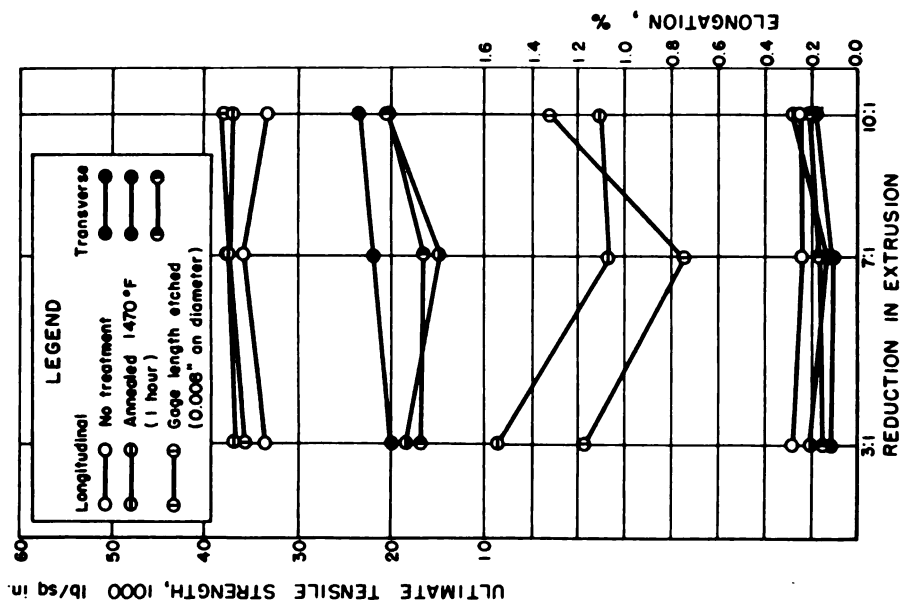


Fig. 1.4.4 — The Effect of Extrusion Reduction on the Ultimate Tensile Strength of Beryllium. Reprinted from MIT Technical Progress Report for the Period February Through April, 1948, MIT-1004, May 24, 1948.

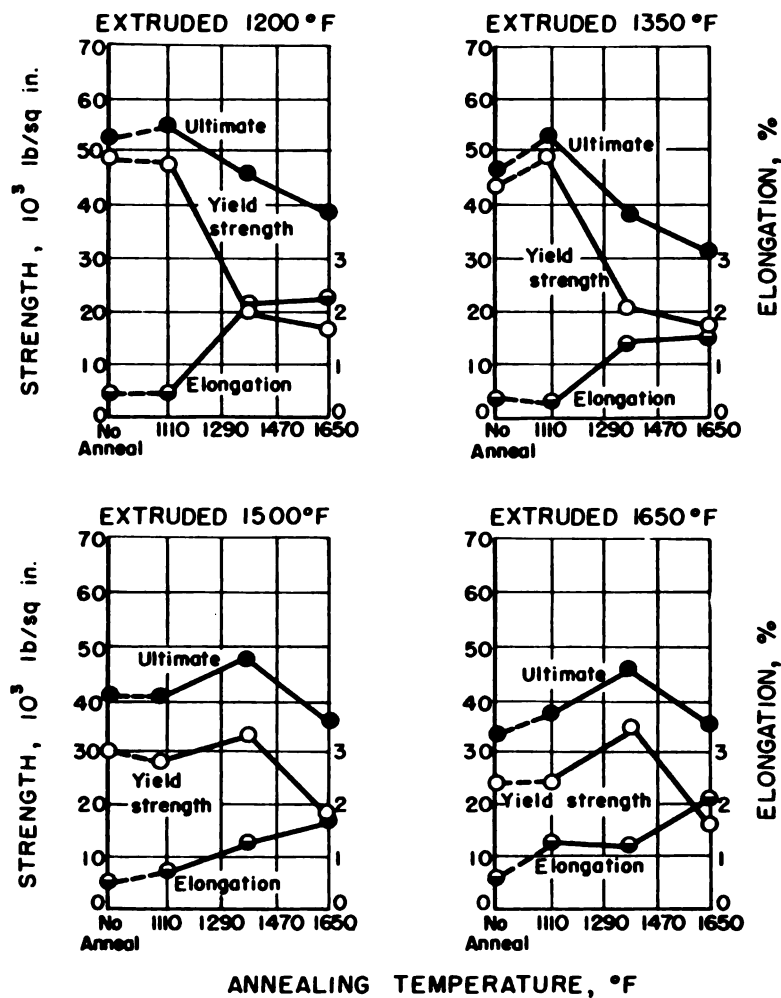


Fig. 1.4.6—The Effect of Annealing Temperature on the Tensile Properties of Beryllium Extruded at Various Temperatures. Reprinted from D. W. Lillie, P. Gordon, and A. R. Kaufmann, *The Mechanical Properties of Beryllium*, J. Met. and Cer., No. 1, July 1948. (Specimens not etched to remove machined surface. Specimens annealed for 3 hr at indicated temperatures.)

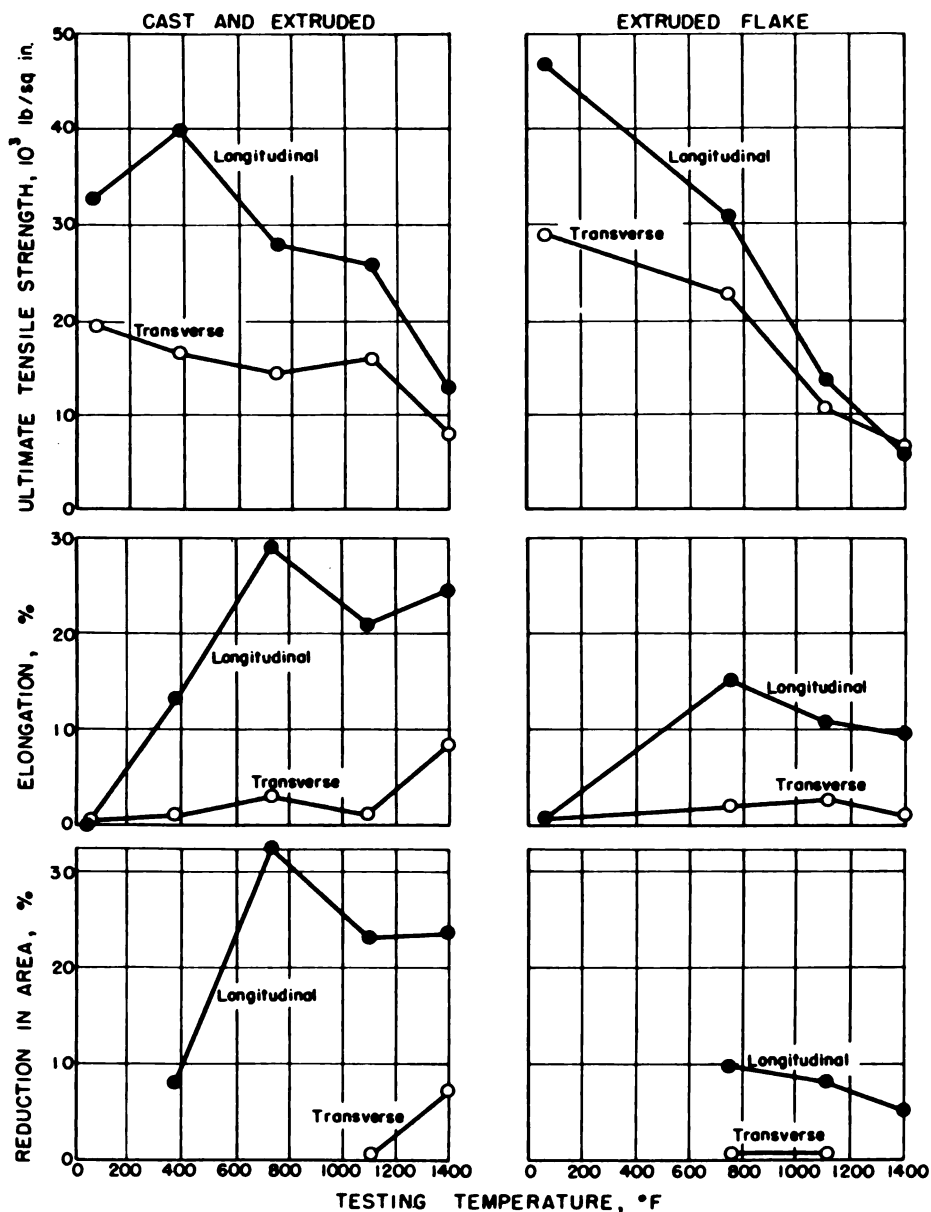


Fig. 1.4.7—Longitudinal and Transverse Tensile Properties of Extruded Beryllium at Elevated Temperatures. Reprinted from D. W. Lillie, P. Gordon, and A. R. Kaufmann, *The Mechanical Properties of Beryllium*, J. Met. and Cer., No. 1, July 1948. (Specimens not etched to remove machined surface.)

Table 1.4.6—Tensile Properties of Beryllium* at 1000°F

Material and treatment	Tensile strength, lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Elongation, %	Reduction in area, %
Hot-pressed QMV, lower limit	24,000	17,000	11.5	23.5
Hot-pressed QMV, upper limit	30,000	24,000	19.8	14.7
Vacuum cast and hot extruded	29,000	23,000	17.0	30.0
Hot pressed and warm extruded	27,000	21,000	15.5	40.0
Hot pressed and hot extruded	33,000	29,000	14.5	35.5

*All specimens etched prior to test

Table 1.4.7—Effect of Strain Rate on the Room-temperature Tensile Properties of Beryllium*

(Condensed from Brush Beryllium Company Report BBC-48, June 26, 1951)

Type of beryllium	Strain rate, in./min movement of testing machine head	Ultimate strength, lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Elongation, %	Contraction in area, %	No. of samples averaged
QMV	0.01	40,300	29,600	2.3	1.8	4
QMV	.1	47,500	34,100	2.6	2.5	5
QMV	1.0	50,300	...	2.2	1.9	5
BP-QRM	0.01	32,900	30,400	1.1	0.8	3
BP-QRM	.1	36,500	35,500	1.1	1.0	3
BP-QRM	1.0	39,700	...	0.3	...	3
BP-QPT	0.01	35,500	28,500	2.0	1.7	5
BP-QPT	.1	36,500	32,200	1.7	1.1	5

*Surface of specimens etched prior to testing

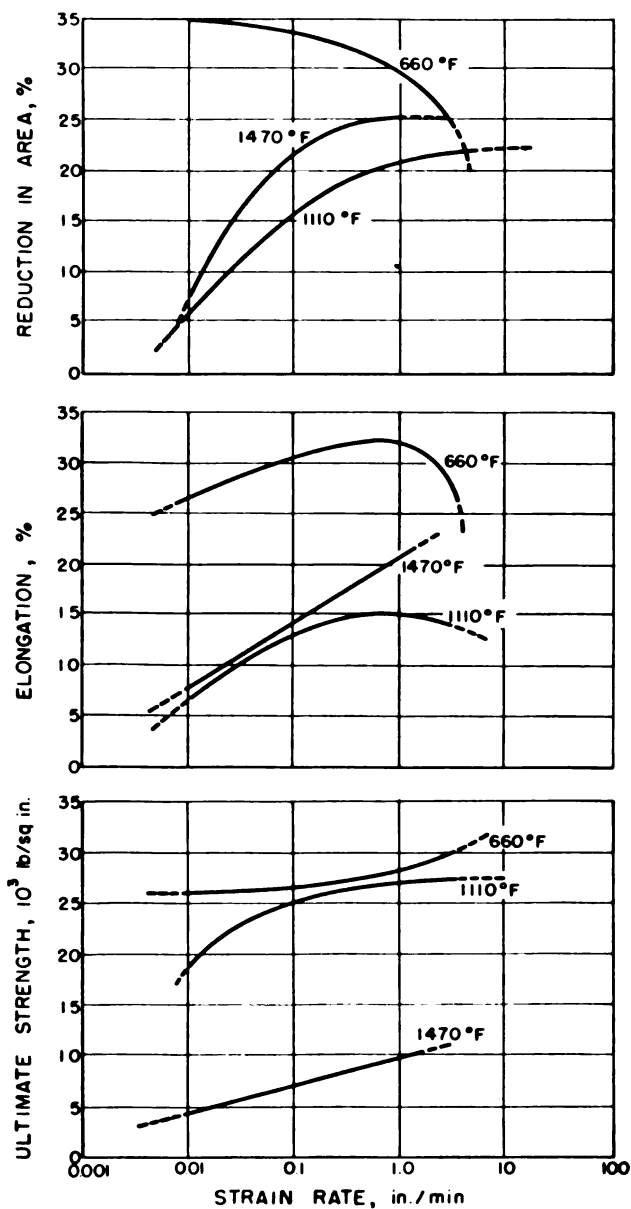


Fig. 1.4.8 — The Effect of Strain Rate on the Tensile Properties of Beryllium at 660°, 1110°, and 1470°F, as Measured in High-temperature Tensile Tests. Reprinted from D. W. Lillie, P. Gordon, and A. R. Kaufmann, *The Mechanical Properties of Beryllium*, J. Met. and Cer., No. 1, July 1948. (Specimens not etched to remove machined surface.)

The compressive strength of polycrystalline beryllium at 1650°F was determined to be 8,270 lb/sq in.

A selected list of room-temperature compression properties for sintered beryllium is given in Table 1.4.8, while Table 1.4.9 presents compressive-strength data for both extruded and sintered beryllium at room temperature.

Table 1.4.8—Compression Properties of Sintered Beryllium*

(Condensed from Brush Beryllium Company Report BBC-48,
June 26, 1951)

Material	BP-QMV	BP-QRM	BP-QPT
Yield strength (0.2% offset), lb/sq in.	24,500	28,900	26,000
Proportional limit, lb/sq in.	3,800	5,900	5,000
Young's modulus $\times 10^{-4}$, lb/sq in.	44.1	44.3	44.3
Poisson's ratio ± 0.005	0.024	0.028	0.025

*Specimens not etched prior to test

Table 1.4.9—Compression Data for Beryllium

Material	Extrusion			Direction of specimen	Average		
	Temp., °F	Ratio	Treatment		Ultimate strength, lb/sq in.	Yield strength (1% offset), lb/sq in.	Deformation, %
Vacuum-cast	1400	4.1-1	As extruded*	Long.	154,000	...	13
				Trans.	47,500	...	3.7
Vacuum-cast	1600	4.1-1	As extruded*	Long.	165,000	...	17
				Trans.	82,000	...	8
Vacuum-cast	1700	4.1-1	As extruded*	Long.	138,000	...	23.5
				Trans.	96,000	...	12.2
Vacuum-cast	1600	4.1-1	As extruded*	Long.	154,500	...	18.3
				Trans.	83,300	...	9.2
Vacuum-cast	1870	6.5-1	As extruded*	Long.	133,000	...	21.8
				Trans.	97,000	...	14.1
Brush Premium Grade Powder (-200 mesh)	1900	33-1	As extruded†	...	178,000	68,800	21
Brush Premium Grade Powder (-200 mesh), hot pressed 1920°F	1850	12.2-1	As extruded*	Long.	208,600	68,000	31.5
				Trans.	152,800	80,900	10.4
			Annealed 1 hr 1470°F*	Long.	206,600	64,700	30.7
				Trans.	153,100	78,300	11.2
Clifton, hot pressed 1850°F	1800	16-1	As extruded†	...	173,500	67,900	29.3
			Annealed 1 hr 1470°F†	...	200,200	58,900	24.2

*Surface preparation unknown

†Specimens etched prior to testing

MODULUS OF ELASTICITY

The generally accepted value of the modulus of elasticity of beryllium at room temperature is about 40×10^6 lb/sq in. Measurements made with a strain gauge on extruded QM beryllium at stresses under 7,000 lb/sq in. gives values between 36 and 45×10^6 lb/sq in. Values reported for the dynamic modulus of elasticity are as follows:

BP-QM beryllium	44.8×10^6 lb/sq in. (Sound velocity method)
QMV beryllium	$42.8-44.7 \times 10^6$ lb/sq in. (Resonance method)
QRM beryllium	$44.4-45.0 \times 10^6$ lb/sq in. (Resonance method)
Extruded flake beryllium	43.0×10^6 lb/sq in. (Sound velocity method)

The effect of temperature on the dynamic modulus is shown in Fig. 1.4.9. It seems likely that the purity and degree of anisotropy of the beryllium test specimens used in the vari-

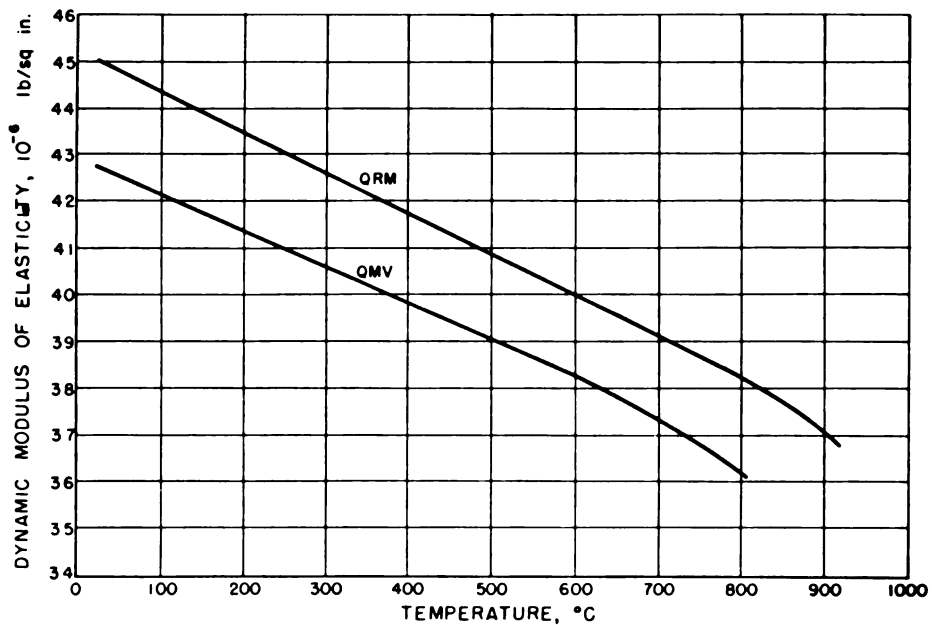


Fig. 1.4.9 — Variation of the Dynamic Modulus of Elasticity for Sintered Beryllium With Temperature. Reprinted from W. W. Beaver and B. C. Raynes, *Mechanical Properties of Beryllium Metal, I. Hot-Pressed Powder, BBC-48*, June 26, 1951. (Specimen etched prior to test.)

ous determinations of the modulus of elasticity have greatly contributed to the scatter in the values obtained.

POISSON'S RATIO

Dynamic measurements of Poisson's ratio yielded values from 0.01 to 0.05. Strain-gauge measurements at stresses under 5,000 lb/sq in. gave values from 0.02 to 0.06, while at stresses up to 12,000 lb/sq in. the ratio measured 0.10 to 0.13. Measurements between 0.15 and 0.195 were obtained on two powder-metallurgy and two extruded samples.

HARDNESS

Hardness measurements of beryllium are dependent on the degree of anisotropy. Hardness measurements on single crystals have given Rockwell B-87 in the 001 direction, and Rockwell B-35 perpendicular thereto. Hardness on a transverse cut on an extruded bar having preferred orientation was Rockwell B-64, while on a longitudinal cut it was Rockwell B-81. Also, beryllium might be expected to be harder than other hexagonal metals because of its small atomic volume. The occurrence of cold working and cracking near Rockwell $\frac{1}{16}$ -in.-ball indentations led to a recommendation for the use of Superficial Rockwell testing. Some room-temperature hardness values for beryllium are listed in Table 1.4.10.

Table 1.4.10—Hardness Values Reported for Beryllium

Material	Rockwell B-Scale		
	Average	Extruded direction	
		Transverse	Longitudinal
Purity 99.5-99.7% Be	62-72*
Flake, extruded 1800°F 16:1			
As extruded	...	69	74
Annealed 1 hr 1470°F	...	71	75
Powder, sintered and extruded 1850°F 12:1			
As machined		86	93
Annealed 1 hr 1470°F		81	91
Extruded			
As extruded		78†	89†
As annealed 1 hr 1470°F		75†	87†
As annealed 1 hr 1830°F		71†	78†
Brush "Process Q"			
As machined	59-83
Annealed 1 hr 1470°F	57-77
Commercial			
Vacuum cast	68-78
Extruded	73-76
Extruded			
Vacuum cast	67
Vacuum cast, annealed	65
Turnings	71
Turnings, annealed	70		
Flake	81		
Flake, annealed	81		

*Converted from BHN

†Converted from Rockwell 30 T-scale

Mutual indentation was used to determine the hardness of beryllium at various temperatures up to 1830°F with the results shown in Fig. 1.4.10.

The effect of quenching from various temperatures on the hardness of sintered and cold-rolled beryllium is shown in Fig. 1.4.11. The minimum value which was found on quenching from 930°F has been substantiated and other work further indicates that slow cooling from 930°F yields a maximum value for hardness among samples slow cooled from temperatures between 480°F and 1830°F.

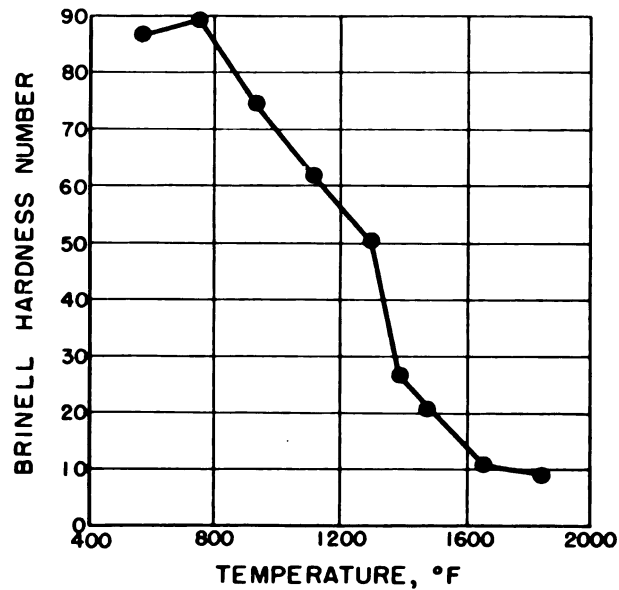


Fig. 1.4.10— Brinell Hardness of Beryllium at Various Temperatures. Reprinted from Progress Report on Metallurgy of Tuballoy, Battelle Memorial Institute, CT-893, BMI-HWR-8, Aug. 10, 1943.

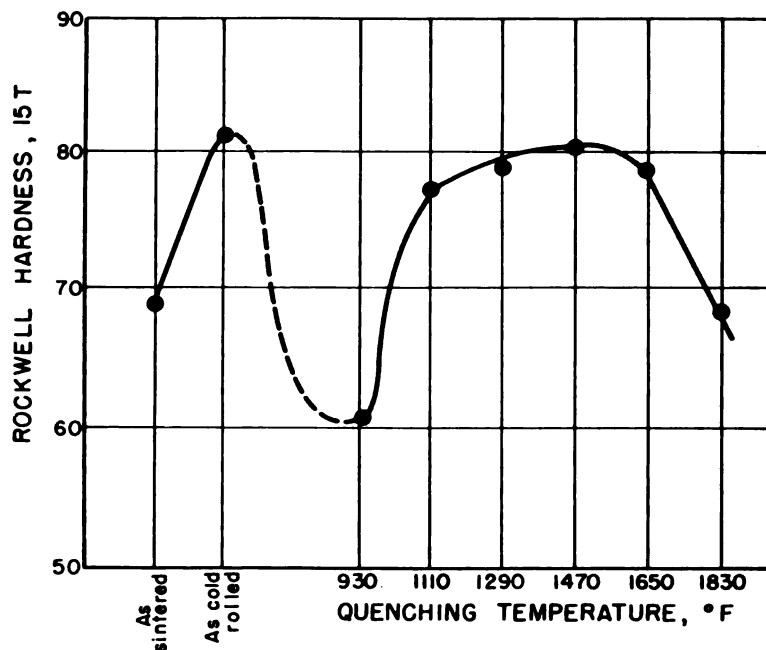


Fig. 1.4.11— Effect of Heat Treatment on the Hardness of Cold-rolled Beryllium. Reprinted from H. H. Hausner and N. P. Pinto, The Powder Metallurgy of Beryllium, AECD-2869, Mar. 24, 1949.

IMPACT STRENGTH

Unnotched beryllium specimens $\frac{7}{32}$ in. \times $\frac{7}{32}$ in. \times 2.165 in. broken on a 2-ft-lb Charpy impact machine at various temperatures gave the results noted in Table 1.4.11.

Table 1.4.11 — Charpy Impact Strength of Extruded and QT Beryllium at Various Temperatures

(The Properties of Beryllium,
BMI-T-14, July 15, 1949)

Temperature, °F	Impact strength, ft-lb	
	Extruded	QT
Room	0.122	0.118
210	.132	.132
390	.249	.180
570	.255	.218
750	1.212	.185
930	0.222	.296
1110	1.357	.189
1290	> 2	.310
1470	> 2	.278

A room-temperature unnotched Charpy impact value of 0.8 ft-lb has been reported for QMV beryllium and a value of 4.1 ft-lb for warm-pressed, hot-extruded, heat-treated beryllium.

SHEAR STRENGTH

Values for the shear modulus have been measured between 17 and 22×10^6 lb/sq in., a value of 19×10^6 lb/sq in. being generally accepted. Measurements of the dynamic modulus using an electrosonic-pulse technique gave values of 21.2 to 21.3×10^6 lb/sq in. for extruded flake metal and Brush BP-QM beryllium, respectively.

The shear properties for pressed and sintered beryllium are given in Table 1.4.12.

Table 1.4.12 — Shear Properties of Pressed and Sintered Beryllium Powder*

(Condensed from Brush Beryllium Company Report BBC-48, June 26, 1951)

Material	Shear modulus, 10^6 lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Ultimate shear strength, lb/sq in.	Remarks on method of obtaining values
BP-QRM	19.0 ± 1.0	16,600	31,400	Torsion
BP-QRM	40,400	Double shear
BP-QMV	21.5 ± 1.0	17,500	38,900	Torsion
BP-QMV	36,800	Double shear
BP-QPT	40,200	Double shear

*Torsion specimens unetched prior to test, others etched

At 1650°F, the shear strength of beryllium has been reported to be 4,900 lb/sq in. Investigations made on single-crystal beryllium indicate the critical-resolved shear stress for twinning to be about 5,000 lb/sq in. compression.

CREEP AND STRESS RUPTURE

Values for extruded-cast beryllium for creep and stress-rupture strengths are shown in Figs. 1.4.12, 1.4.13, and 1.4.14. Hot-extruded QMV beryllium was tested in sodium at 1000°F and the results are given in Table 1.4.13.

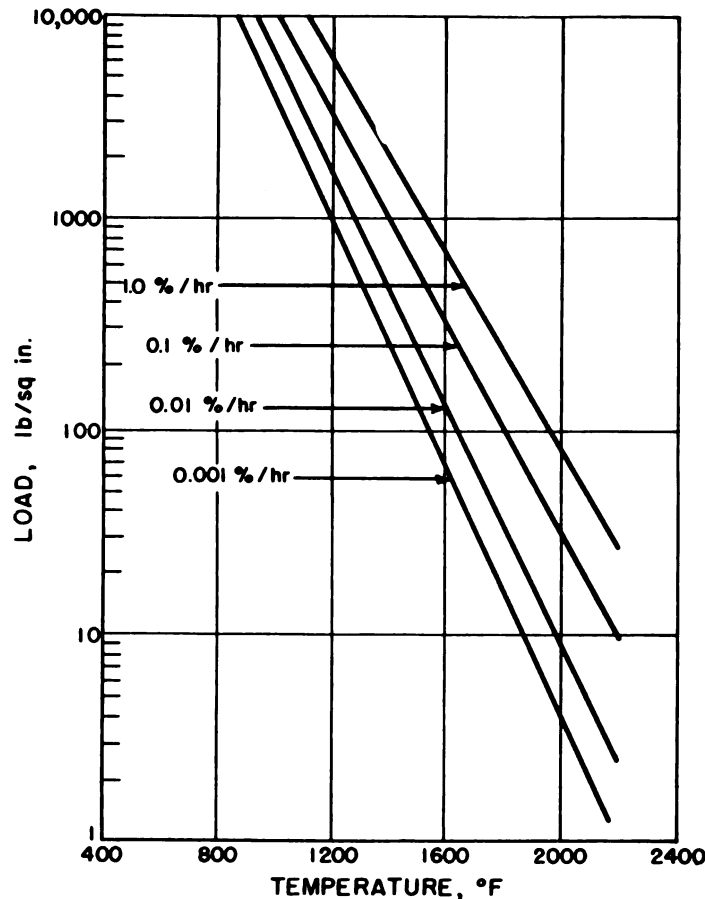


Fig. 1.4.12—Load to Produce Creep Rates of 1.0, 0.1, 0.01, and 0.001 Percent per Hour at Temperatures Between 900° and 2200°F for Beryllium. Reprinted from D. W. Lillie, P. Gordon, and A. R. Kaufmann, *The Mechanical Properties of Beryllium*, J. Met. and Cer., No. 1, July 1948. (Specimens not etched to remove machined surface.)

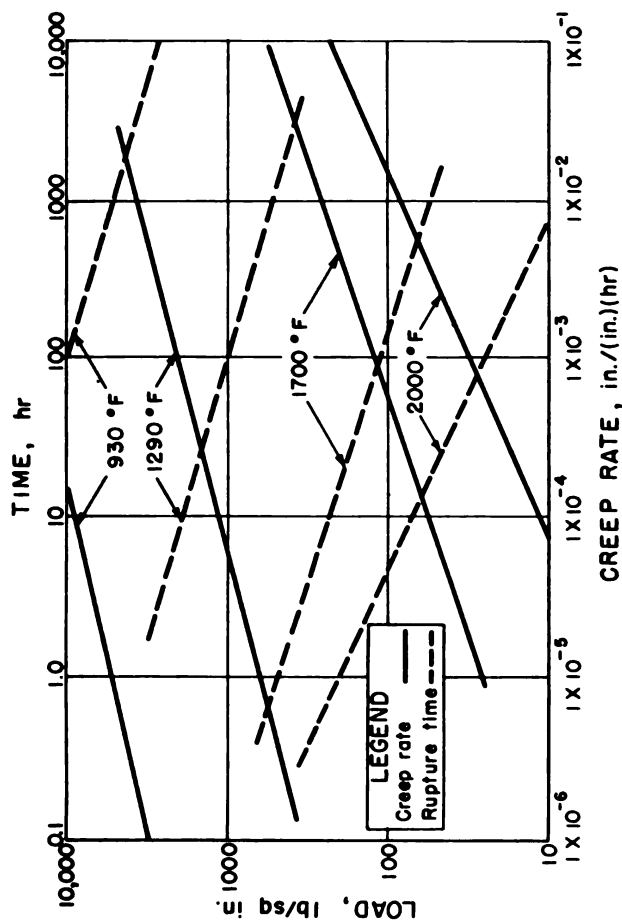


Fig. 1.4.14—Stress-rupture and Creep Data for Beryllium. Reprinted from D. W. Lillie, P. Gordon, and A. R. Kaufmann, *The Mechanical Properties of Beryllium*, J. Met. and Cer., No. 1, July 1948. (Specimen not etched to remove machined surface.)

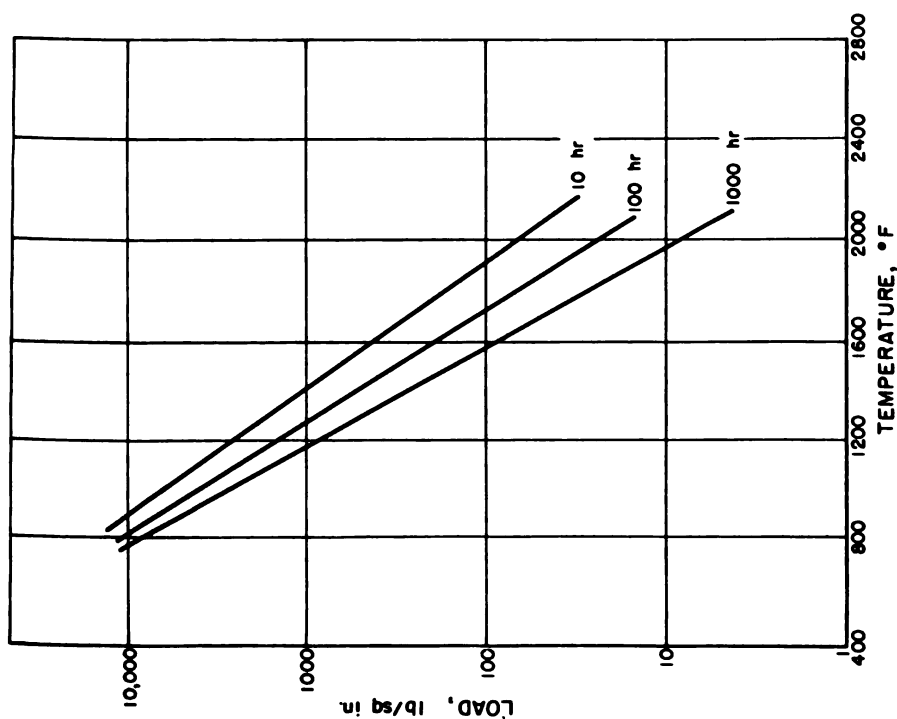


Fig. 1.4.13—Load to Produce Rupture of Beryllium in Rupture Times of 10, 100, or 1000 hr at Temperatures Between 800° and 2100°F. Reprinted from D. W. Lillie, P. Gordon, and A. R. Kaufmann, *The Mechanical Properties of Beryllium*, J. Met. and Cer., No. 1, July 1948. (Specimens not etched to remove machined surface.)

**Table 1.4.13 — Stress-rupture Data for QMV
Beryllium in Sodium at 1000°F**

(Reactor Materials Progress Report,
KAPL-655, Sept., Oct., and Nov. 1951)

Stress, lb/sq in.	Time to fail, hr	Elongation, %
10,000	4	8
6,000	15	10
4,000	235	4
3,000	584	6
2,500	5,724	4
2,000	4,536	2

TORSIONAL BEHAVIOR

Figure 1.4.15 shows the maximum twist to rupture and the maximum torque at rupture for small beryllium rods at various temperatures. The effect of the rate of strain on the maximum twist to rupture and the maximum torque at rupture at various temperatures are shown in Fig. 1.4.16. It will be noted in Fig. 1.4.15 that the ductility goes through a maximum and minimum with increasing temperature similar to the behavior exhibited during elevated-temperature tensile tests, while the strength decreases somewhat linearly with increasing temperature in both types of tests.

THERMAL-SHOCK TESTS

The results of thermal-shock tests conducted by quenching in molten sodium at 660°F from 990°F are shown in Table 1.4.14.

MELTING AND CASTING

Beryllium oxide crucibles are probably the most satisfactory for melting beryllium. Prefiring to 3270° to 3450°F improves their resistance to thermal shock. Magnesium oxide crucibles have been used successfully, but they must be of high purity to avoid iron and silicon pickup in the beryllium. Fluoride fluxes attack both types of crucible. Graphite crucibles are hazardous because of the exothermic reaction between beryllium and carbon at a temperature less than 200°F above the melting point of beryllium. Graphite-bonded silicon carbide crucibles (Tercod) can be used if the glaze is first removed with molten cryolite and an oxide coating then added by melting a wash heat of beryllium. However, the use of this type of crucible in a pure argon atmosphere, or in a vacuum, is reported to be unsatisfactory.

Vacuum-melting beryllium has been developed satisfactorily. This is carried out in a vacuum of from 100 to 500 μ using induction heating. One of its chief advantages lies in the ready elimination of the volatile impurities such as fluorides, chlorides, magnesium, and sodium. Also, melting in an argon atmosphere, or under an argon blanket, has been practiced with considerable success. Nitrogen reacts excessively with molten beryllium, but hydrogen has been used as a protective atmosphere to a limited extent.

In the casting of beryllium, graphite is used most generally as the mold material. Quality variations affect its suitability for this purpose, however. A recommended good grade

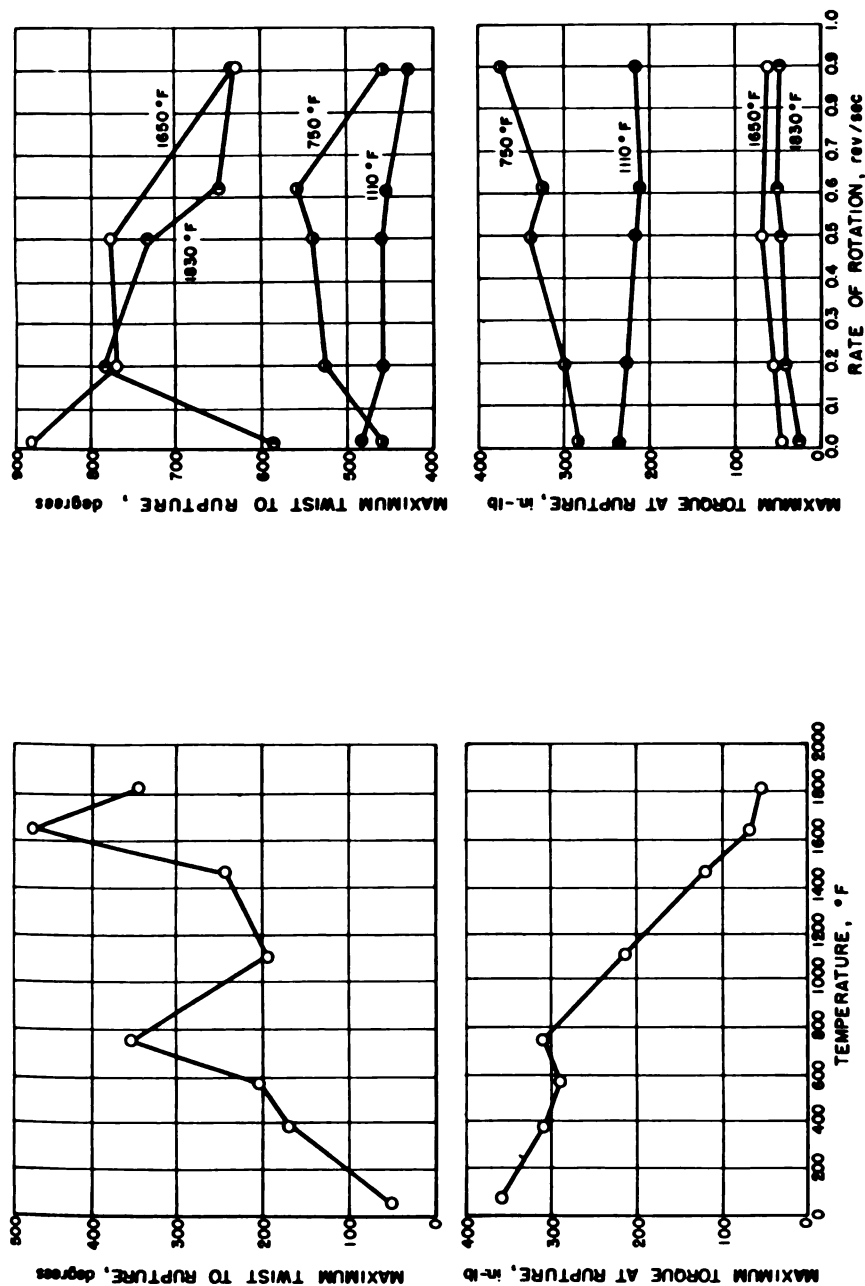


Fig. 1.4.15—The Effect of Temperature on the Maximum Twist to Rupture and Maximum Torque at Rupture for Torsion Tests on Beryllium Rods. Reprinted from MIT Progress (A-1) Report for the Period December 1946 to Mar. 1947, CT-3804, May 28, 1947. (Specimens were rods 0.357-in. diameter and 1.0-in. gauge length. Rate of strain was 0.1 rev/sec. Material was vacuum cast and extruded. Specimens not etched to remove machined surface.)

Fig. 1.4.16—Effect of Strain Rate on Maximum Twist to Rupture and Maximum Torque to Rupture for Torsion Tests on Beryllium Rods. Reprinted from MIT Progress Report for August and September, 1947, MIT-1000, Nov. 25, 1947. (Specimens were vacuum cast and extruded rods 0.357 in. in diameter and with a 1.0-in. gauge length. Specimens not etched to remove machined surface.)

Table 1.4.14 — Thermal Shock Resistance of Beryllium Fabricated by Various Methods Quenched from 990°F to 660°F

(Adapted from Reactor Materials Progress Report, KAPL-655, Sept., Oct., and Nov. 1951)

Method of fabrication	Original diameter, in.	Results*
Hot pressed	2	Cracked and checked in 300-400 cycles
Hot pressed	1½	O.K. after 500 cycles
Hot pressed and hot extruded	1½	Cracked and checked in 100-200 cycles†
Hot pressed and hot extruded	2½	O.K. after 200 cycles
Vacuum cast and hot extruded	2½	Cracked in first 100 cycles
Cold compacted and hot extruded	1½	Cracked at top in 100-200 cycles
Hot pressed and warm extruded	1	Cracked in 100 cycles

*Specimens examined after each 100 cycles

†Two specimens, both cracked in 100-200 cycles

is the National Carbon Company's "CS" Grade. Among other mold materials, which have been used with varying degrees of success, are beryllia-coated steel molds; beryllia-coated Alundum thimbles; rammed molds, based on magnesia and zirconite sands; and oxychloride-bonded magnesia-sand molds, which were baked at high temperatures prior to use. Ceramic hot tops are recommended. Centrifugal castings up to 52 in. in diameter have been cast successfully using beryllia-coated steel molds.

The cracking of beryllium castings during cooling is a considerable problem. It may be minimized by controlling the rate of cooling, the use of collapsible molds where there is any restriction to normal shrinkage, or design to eliminate any such restriction, and stripping the casting from the mold as soon as possible after pouring. Heating the top of the mold to 1110°F and the bottom to 930°F and pouring at 2550°F has been recommended. Iron, above 0.2 to 0.3 percent, is reported to increase the possibility of cracking, while the addition of 0.25 to 0.50 percent aluminum appears to promote soundness in the castings. Slow cooling of the casting leads to extremely large grain size with resultant poor properties. Hydrogen from water vapor also produces unsoundness, which necessitates the drying of the apparatus and raw materials used in the melting and casting.

FORMING AND FABRICATION

EXTRUSION

The extrusion process has been used extensively to produce beryllium bars, tubes, and shapes. The starting material is generally a vacuum-cast billet, but compacted powder or flake beryllium may be extruded with equal facility. In the general process, the billet is "canned" in a $\frac{1}{16}$ - or $\frac{1}{8}$ -in. mild-steel jacket, the forward end of the billet having been machined to a truncated cone and the space so produced filled with a soft-iron introductory cone, tack welded to the jacket. This cone facilitates the flow of the jacket, which is copper plated to minimize adherence to the die. The use of a glass lubricant has been reported but generally is not employed. Customarily, extrusion may be carried out at 800°F or in the range 1500° to 2000°F, the usual temperature being about 1830° to 1920°F, employing a bell-shaped die, a steel cutoff block, a graphite dummy block, and a final steel block next

to the ram. The hot-top end of the billet is forward to minimize the extent of pipe defects and splitting. Straightening is done while still red hot.

Bare extrusion, which allows closer dimensional control, has been successful. At higher temperatures, refractory alloy dies are required to prevent seizure, but at 800°F 18-4-1 tool-steel dies have been satisfactory. About 20 percent more power is required to extrude bare. The "Extru-Powder" process in which a sintered-powder billet is extruded at 800°F has been used to produce a variety of shapes. Bare extrusions require a graphite-entering and lubricating cone. Multiple-hole dies have been used in the extrusion of small, round rods.

Extrusion ratios of 16:1 are not uncommon. At 800°F, bare extrusion is limited to about 9:1 because of die breakage. The larger reductions are preferred. Acceptance tests for detecting undesirable longitudinal inclusions in extruded beryllium consist of the following: end cropped and deep etched with dilute sulfuric acid, transverse section fractured, and quenching from a red heat. Cracks in the original billets are not completely healed by extrusion. Damaged surface layers may be removed by etching.

All extrusions below the recrystallization temperature of about 1340° to 1470°F are in the cold-worked condition. Extrusions also show a high degree of preferred orientation. The 0001 (basal) planes and the 10 $\bar{1}$ 0 direction tend to parallel the extrusion axis. The preferred orientation persists on annealing even up to 1830°F, although gross fibering virtually is eliminated by annealing at temperatures above 1380°F.

DRAWING

So far as is known, the present nonductile beryllium cannot be drawn at room temperature.

ROLLING

Beryllium cannot be rolled to any degree at room temperature. Rolling as low as 800°F with the beryllium open to the atmosphere results in extensive embrittlement. The usual method is to jacket the metal in low-carbon steel, or some other suitable material, using a parting compound when necessary to prevent interdiffusion at the rolling temperature.

Rolling at temperatures below the recrystallization temperature results in a cold-worked metal, i.e., below 1340° to 1470°F. For final dimensional accuracy temperatures as low as 660°F have been used. At 800°F, a reduction of 56 percent was secured before cracking.

To minimize grain growth, rolling just above the recrystallization temperature is recommended. Reductions of 83 and 89 percent before cracking have been obtained at 1470° and 1560°F, respectively. Single-pass reductions of 45, 56, and 74 percent have been reported on extruded beryllium at 1400°F from an initial 0.401-in. thickness. Rolling at 1600° to 1800°F has been satisfactory. If rolling to thin sections, slow cooling and extreme care during jacket removal are advised.

The preparation of thin foil, e.g., 0.002-in. or less, has been reported by several different fabricators. In general, the processes were similar and consisted of rolling at 1400° to 1560°F to a thickness of 0.015 to 0.060 in., stripping, rejacketing in nickel or stainless steel, and rolling to the final size, or close enough to it to permit sizing the foil with a final low-temperature rolling between stainless steel plates.

FORGING, PRESSING, AND COINING

The forging characteristics of beryllium have been compared to those of magnesium. Simple forging, such as single-stroke upsetting, can be done at 1500° to 2000°F provided the beryllium is encased in $\frac{1}{2}$ in. of 1020 steel. Fair success has been achieved in die forging at 1800°F with dies designed to keep the metal under compression. Hot coining, using Oil Dag lubrication, has been reported.

POWDER METALLURGY

Process "Q" beryllium, produced by the Brush Beryllium Company, is a powder-metal-lurgy product manufactured by hot pressing powdered beryllium into billets, or by cold pressing and sintering. Powder-process beryllium metal contains considerably more oxygen than the vacuum-cast parent metal. During the attrition milling to minus 200-mesh powder in an atmosphere of nitrogen, the beryllium oxide content increases from about 0.2 percent to about 2.0 percent, or more. Apparently, even during storage under commercially pure argon, the oxide content of the powder continues to increase somewhat. The average particle size of the minus 200-mesh powder is about $15\ \mu$. A screen analysis of 96 percent minus 200-mesh beryllium powder showed about 63 percent to be minus 325-mesh and 57 percent minus 400-mesh.

In cold pressing minus 200-mesh beryllium powder, the maximum compact density is reached at about 140,000 lb/sq in. Little sintering, either in vacuum or in argon, appears to occur under 1830°F. Argon-sintered compacts are more brittle than those sintered in vacuum, and their densities are dependent on the compacting pressure used, while the densities of vacuum-sintered compacts are quite independent of the compacting pressures as indicated in Fig. 1.4.17. The change in electrical resistivity without a corresponding

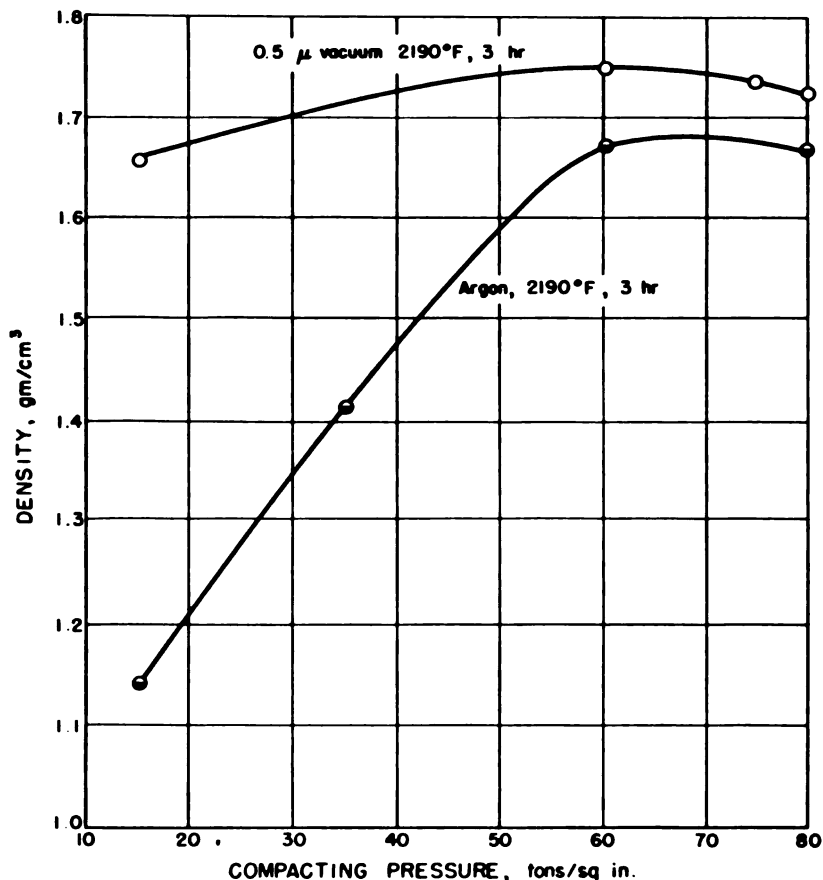


Fig. 1.4.17 — The Effect of Compacting Pressure and Sintering Atmosphere on the Density of Minus 200-Mesh Beryllium Powder. Reprinted from *Beryllium and Beryllium Oxide Production and Development*, November 21, 1949, NYO-110, June 9, 1950,

change in density, which occurs during the vacuum sintering of beryllium powder, is shown in Fig. 1.4.18. This interesting phenomenon, which does not occur when sintering in argon, has been ascribed to an increase in contact area between the grains brought about by the migration of beryllium atoms through evaporation and condensation. Evaporation during

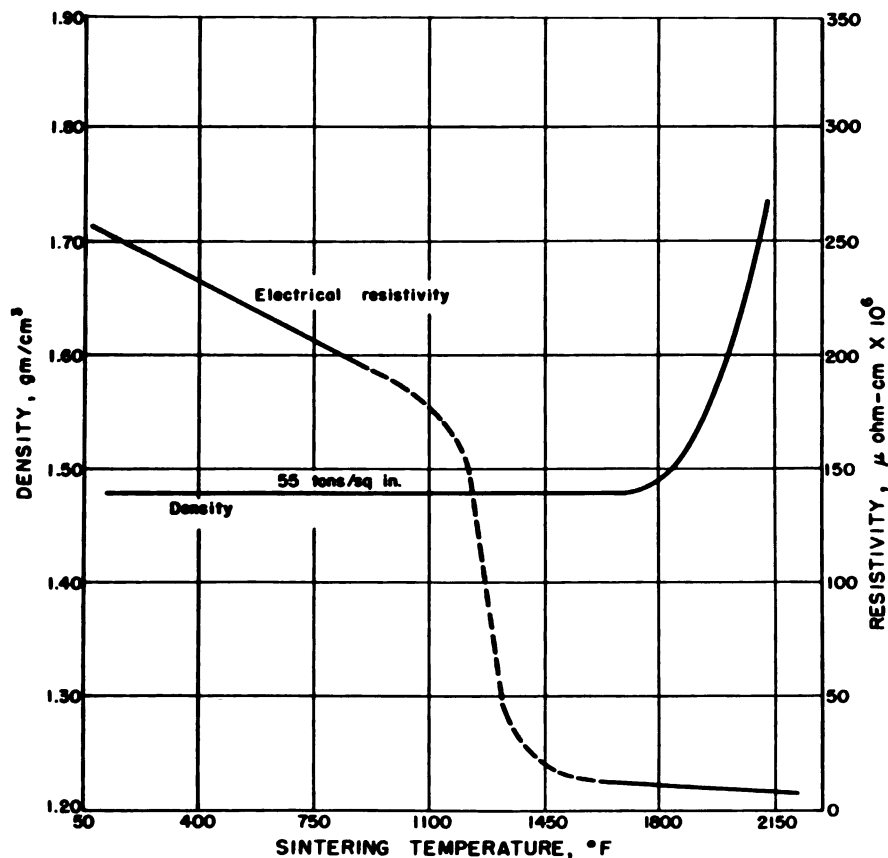


Fig. 1.4.18—The Resistivity and Density of Vacuum-sintered Beryllium Versus Sintering Temperature. Reprinted from H. H. Hausner and N. P. Pinto, *The Powder Metallurgy of Beryllium*, AECD-2869, Mar. 24, 1949. (Measurement made at room temperature.)

the vacuum sintering of beryllium accounts for a large loss in weight, e.g., possibly up to 25 percent depending on the ratio of surface area to volume, which can be reduced by covering the specimens with the oxide powder. Densities averaging 1.70 and 1.75 have been reported after sintering for 3 hr at 2190°F and 2255°F, respectively.

Massive beryllium may be produced by pressing the powdered metal at about 800°F, at which temperature a maximum tensile ductility is observed. This is known as warm pressing to differentiate it from the hot-pressing process. The powder is loaded in an 18-4-1 tool-steel die and compressed at 200,000 lb/sq in. at the above temperature. Exceptionally good strength is obtained in the resultant metal.

Various techniques of hot pressing beryllium powder have been reported at temperatures of 1830° to 1920°F and pressures from 75 to 1000 lb/sq in. Both simple and complicated shapes, e.g., finned tubing and fluted spacer rods, have been fabricated by loading the beryllium powder in a thin, pliable, low-carbon steel housing, evacuating this envelope to

about 200 μ , putting it under an external pressure of argon gas at about 100 lb/sq in. and sintering at 1830°F. Another hot-pressing method consists of inductively heating the powder at 1830° to 2010°F in a glass-coated mild steel can under a pressure of 750-1000 lb/sq in. for one-half hour.

JOINING

SOLDERING

It has been reported that beryllium may be soldered in the normal manner after it has been coated with copper. One method, which has been described, is to paint the beryllium with a paste of CuCl_2 in turpentine and heat to 800°F to get a copper deposit on the beryllium. The soldering of beryllium electroplated with copper has not been reported.

BRAZING

Beryllium has been furnace brazed successfully in an argon atmosphere at temperatures between 1400° to 1600°F using foils of aluminum and the following aluminum alloys (in weight percent): 88.3 Al-11.7 Si, 90 Al-10 Ag, 96 Ag-4 Al, and 98 Al-2 Mg. Attempts to braze with silver, gold, bismuth, cadmium, iron, indium, magnesium, nickel, lead, tin, zinc, silver solder, and lead-tin solder are reported to have been unsuccessful.

Satisfactory beryllium brazing has been accomplished with aluminum filler rod. The use of copper filler rod and copper foil in furnace brazing are reported to be unsatisfactory, although the use of "Phos Copper" without flux and the use of copper to braze beryllium foil to Monel has been described as successful. The suitability of copper for brazing probably requires further investigation. Moderate success has been reported in recent vacuum-furnace brazing tests using silver or the silver-copper eutectic alloy to join beryllium to itself and to stainless steel, Monel, and nickel.

Beryllium can be roll brazed to beryllium at 1550° to 1600°F by employing an intermediate layer of aluminum or an alloy of 99.2 Al-0.8 Zr. Considerable rolling reduction is required.

WELDING

The welding of $\frac{3}{16}$ -in. beryllium plates without filler rod using a helium-shielded arc and straight polarity has been described in the literature.

The pressure welding of beryllium has been accomplished at temperatures from 1920° to 2280°F using the differential thermal expansion of graphite and beryllium to produce pressure at the welding temperature. Successful welding at 2010°F has been reported where pressures of 500 lb/sq in. were applied to the surfaces to be joined.

Beryllium has been self-welded in 1 to 3 hr at 2200°F in vacuum or argon with good resistant bonds. Fixtures of graphite or oxidized beryllium were used.

MACHINING

Beryllium is unusually prone to surface damage during machining. Generalized cracking may occur beneath the machined surface to depths several times the depth of cut. For example, a 0.030-in. shaper cut with a 0.010-in. feed caused cracking to a depth of 0.125 in. below the machined surface.

The Norton Company has developed a special abrasive wheel to grind beryllium without producing cracks. It is designated No. 57A46-G12VBEP No. 24 treated. The sensitivity to grinding cracks apparently varies with the history of the beryllium in the following order of increasing sensitivity: extruded and rolled, extruded, and cast. For machining, carbide-

tipped tools generally are preferred but not required. Comparative machinability tests based on the wear of high-speed steel shaper tools showed that powder-process ("Q") beryllium rated better than did either extruded or cast metal, the latter being the poorest of the three types. The rate of tool wear on extruded beryllium was less when machined in the direction of extrusion than when machined transverse to the extrusion direction.

Table 1.4.15 gives the recommended turning and cutting speeds for beryllium, while Table 1.4.16 gives data on drilling beryllium.

Table 1.4.15 — Recommended Turning and Cutting Speeds for Beryllium

Diameter of work, in.	Spindle speed, rev/min	Cutting speed, in./min	Feed, in./rev
$\frac{1}{4}$	438	28.7	0.0015
$\frac{1}{2}$	438	57.4	.0030
1	277	72.5	.0030
2	171	89.5	.0060

Table 1.4.16 — Optimum Conditions for Drilling Beryllium

Tool	Spindle speed, rev/min	Feed, in./rev	Coolant	Coolant pressure, lb/sq in.
Carbide tipped, work only turning	1400	0.006	50-50, paraffin and sulfur- base oil	500
High-speed steel, work only turning	1000	.00028	Cut max	700
High-speed steel, work and tool turning	1486		Sulfurized oil with 2% Oil Dag	22

HEAT TREATMENT

RECRYSTALLIZATION AND GRAIN GROWTH

The major effects of heat treatment of beryllium are recrystallization and grain growth. The recrystallization temperature and time vary with the degree of prior deformation as shown in Fig. 1.4.19. Brinell impressions were used in this work to obtain the deformation because of the difficulty of cold working the brittle metal at room temperature. The lowest recrystallization temperature appears to be about 1290°F, although generally it is considered to be around 1400°F. However, recrystallization has been reported in beryllium extruded at 630°F. Preferred orientation introduced by extrusion or rolling persists on annealing up to 1830°F, although recrystallization eliminates gross fibering as low as 1335°F. In heat treatments at 480°, 930°, 1380°, and 1830°F, a maximum hardness occurred on slow cooling from 930°F, while a minimum hardness resulted from quenching at the same temperature. Unidentified impurities may have caused this effect.

Few data are available on the grain growth of beryllium. Figure 1.4.20 presents a series of isothermal grain-growth curves between 1650° and 2190°F.

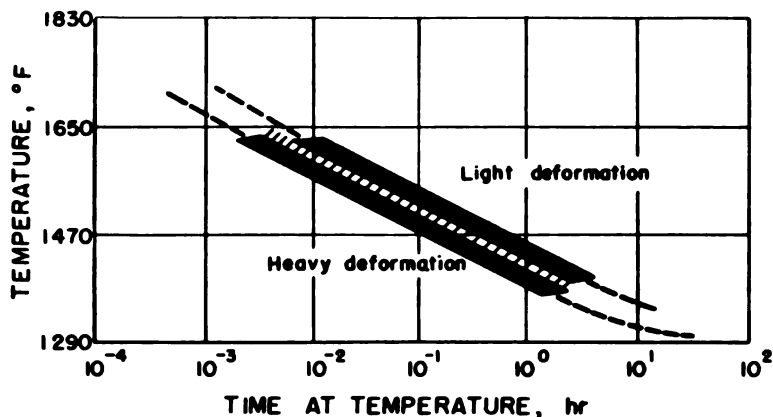


Fig. 1.4.19 — Time-temperature Relationship for Recrystallization of Beryllium. Reprinted from MIT Progress Report for Month of October, 1944, CT-2387, Dec. 6, 1944.

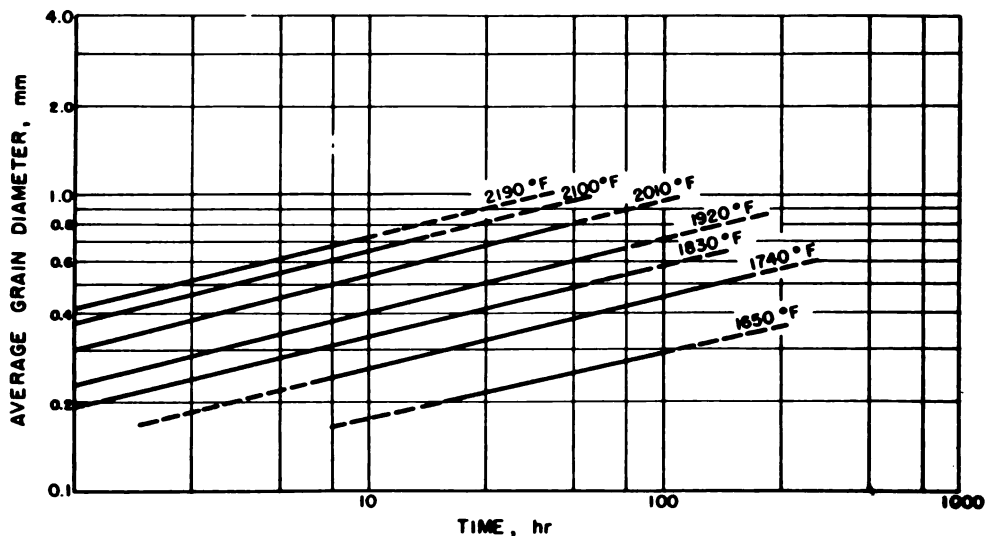


Fig. 1.4.20 — Isothermal Grain-growth Curves for Beryllium of Initial Grain Diameter of 0.193 mm. Reprinted from T. J. Dunkerley, et al., Recrystallization and Grain Growth Characteristics of Beryllium and Zirconium, Univ. Pa. No. 9, June 12, 1950. Extrusion Ratio 4:1 at 1900°F, Annealed 1830°F. Grain Count Normal to Extrusion Axis.

THERMAL CYCLING AND STABILITY

Samples of extruded beryllium cut both normal and parallel to the direction of extrusion showed negligible dimensional changes and warping after 500 cycles between 300° and 930°F.

CORROSION BEHAVIOR

ATMOSPHERIC

Severe corrosion of beryllium does not occur in air at 750°F in 200 hr. Noticeably severe corrosion of extruded vacuum-cast beryllium is reported to occur in air in 60 hr at 1290°F, in 12 hr at 1470°F, and in 1 hr at 1650°F. A white film forms on the surface of beryllium after 1 hr in air at 1470°F, while 1 hr at 1830°F produces a heavy, white scale. The scale, when analyzed, showed only 0.75 percent Be_3N_2 . However, according to some reports, the resistance of beryllium to oxidation at 1290°F appears to equal that of 18-8 stainless steel. The oxidation resistance of extruded vacuum-cast beryllium is reported to be superior to either the extruded flake or the powder-metallurgy (Q-metal) product at 1290°F and 1470°F in air.

Between 660°F and 1740°F, the beryllium-oxygen reaction follows the parabolic rate law except at the beginning of the reaction. In the range 1380° to 1740°F, the energy of activation is 50,300 cal/mole. The usual oxide is BeO , although BeO_2 has been observed and found to be unstable.

The beryllium-nitrogen reaction between 1110° and 1700°F follows the parabolic rate law and an activation energy of 75,000 cal/mole has been determined over the range 1340° to 1700°F. The nitride, Be_3N_2 , has been identified.

No reaction between beryllium and hydrogen was found in the range 572° to 1620°F.

At 1950°F in air, a beryllium specimen with a surface area of 8.505 cm^2 was found to gain weight at the following rate: $\frac{1}{2}$ hr 0.0014 gm, 1 hr 0.0023 gm, $1\frac{1}{2}$ hr 0.0040 gm, and in 2 hr 0.0057 gm.

WATER

Beryllium appears to be definitely inferior to zirconium in corrosion resistance to water. The corrosion rate is increased when the pH value is raised above 6.5 or if the extruded surface has been chemically etched prior to exposure. The corrosion rate of extruded beryllium appears to be less erratic for material extruded at higher ratios.

Corrosion tests in boiling water indicate that "Process Q" and extruded flake beryllium are inferior to extruded vacuum-cast metal. Sintered and extruded metal showed no evidence of corrosion after 144 hr exposure and only a few pits in 288 hr, although weight gains varying from 2 to 140 mg/dm^2 have been recorded after 150 hr.

In 570°F water, considerable variation has been found in corrosion resistance. Long-time corrosion tests of sintered (QM and QRM) and extruded beryllium in 600°F and 525°F water indicated poor corrosion resistance in the former and good corrosion resistance to the latter. In 600°F distilled water, the hot-pressed metal was superior to the extruded vacuum-cast metal and at 570°F extruded sintered metal was found to be better than as-cast or single-crystal beryllium. The attack by 572°F distilled water did not appear to be progressive. Tests at 525°F in distilled water for 2 weeks' duration on different grades of beryllium gave the following results: QM 1.0 to 144.5, QRM 2.3 to 18.1, and QMV 0.0 to 5.0 $\text{mg}/(\text{dm}^2)(\text{mo})$.

Vacuum-cast and extruded beryllium tested in simulated pile-cooling water (demineralized water with added H_2O_2) indicated that the corrosion rate of the material was sensitive to minor changes in the media; that annealing did not effect the corrosion rate during

long-time exposure, but caused a higher rate during short exposures; and that there were no significant differences in corrosion rate over the entire extrusion length. A change from 0.0005 M to 0.005 M H_2O_2 increased over-all corrosion but decreased pitting attack. The weight loss observed in 0.005 M H_2O_2 at 185°F during a 12-month exposure was at a rate of 0.5 to 11.3 mg/(dm²)(mo), but in 7 days at 525°F and 840 lb/sq in., a weight gain of 23 to 827 mg/(dm²)(mo) was reported. After 750-1500 hr in a 0.002-0.006 M H_2O_2 solution at 185° to 200°F, no evidence of stress-corrosion cracking was found in beryllium stressed at 90-95 percent of the yield strength, but a pitting-type corrosion was observed.

The following corrosion inhibitors have been recommended for use in simulated pile water: 2 to 5 ppm and 10 to 40 ppm sodium nitrate for extruded beryllium; 30 to 40 ppm sodium nitrate at pH 6 for extruded beryllium; 5 ppm sodium chromate at pH 7.5-8.0 for extruded beryllium; and sodium chromate for Process-Q beryllium.

The presence of copper or chlorine in static distilled water plus 0.005 M H_2O_2 at 185°F caused deep pitting in QRM beryllium. The maxima for these ions was set at 0.05 ppm for copper and 0.2 ppm for chlorine. Aluminum ions appeared to have no adverse effect in concentrations between 0.03 and 1.24 percent aluminum.

A beryllium tube at 190°F showed no corrosion in simulated pile water (0.005 M H_2O_2 plus 5 ppm $\text{Na}_2\text{Cr}_2\text{O}_7$, pH 7) flowing at 30 ft/sec. Beryllium samples in oxygen-saturated water flowing with a surface velocity of 27 ft/sec exhibited severe intergranular corrosion with actual decomposition occurring during a 19.5-day test.

Type-356 aluminum coupled with beryllium increased the corrosion rate of beryllium in simulated pile-cooling water. Typical corrosion results for beryllium in such water at 185°F for 60 days were as follows:

Material	Weight losses, mg/(dm ²)(mo)	
	0.005 M H_2O_2	0.0005 M H_2O_2
Be	12.2 to 204	-6.0 to 34.7
Al	-0.3 to 89.3	-5.9 to 18.2

Among these coupled specimens, the machined and heat-treated or etched specimens had the lower and more uniform corrosion rates.

LIQUID METAL

At 1830°F, bismuth is reported to attack beryllium fairly uniformly. After 4 hr, the beryllium had lost 21 mg/cm². No attack was found in 24 hr at 1290°F.

Gallium severely attacked beryllium at 1500°F and attacked it slightly at 1000°F. At 1100°F, the rate of attack appeared dependent on the surface condition of the beryllium, fine-grained beryllium being attacked more readily than the coarse grained.

Lead did not attack beryllium in 24 hr at 1290°F. Beryllium is reported to have shown fair resistance to lead during a 40-hr exposure at 1830°F.

Lithium severely attacked extruded beryllium at 1830°F with the following results:

Exposure time, hr	Weight change, mg/cm ²	Penetration, mils
4	-17	3.7
40	-68	14.7

Beryllium exposed to lithium at 930°F for 1-month showed a loss of 1.63 mg/cm²/mo.

Magnesium attacked beryllium to a slight extent at 1472°F.

Sodium and its alloys with potassium and calcium apparently cause an oxidation type of corrosion on beryllium, the rate being affected by the oxygen content of the liquid metal. In static tests, the initial oxide coating offers some protection, but this protection is not

present in dynamic tests. At 1110°F, extruded beryllium was not attacked by oxygen-free NaK for at least 6 days, but when oxygen was present, there was considerable attack. The limitation of oxygen in sodium to less than 0.01 percent has been advised to reduce the corrosion of beryllium. Sodium which has been treated with up to 2 percent calcium has been found to be less corrosive on beryllium. In sodium, powder-process beryllium generally corrodes at a faster rate than does the vacuum-cast metal. Table 1.4.17 presents some corrosion-erosion and corrosion data for beryllium in sodium and its alloys with potassium or calcium.

Tin did not attack beryllium in 24 hr at 1290°F.

Table 1.4.17—Corrosion of Beryllium in Sodium and Its Alloys

(Based on The Properties of Beryllium, BMI-T-14, June 1949
and KAPL Memos JPH-23, 25, 28, 29, 30; Apr. to Oct. 1948)

Material	Media	Container	Temperature, °F	Time	Velocity	Wt. loss, mg/(dm ²)/(hr)	Erosion, mils/month
Brush QT No. 1	NaK	...	800, max 900	49 hr	10 ft/sec	0.14	0.233
Brush QT No. 2	NaK	...	800, max 900	49 hr	10 ft/sec	.77	1.201
Extruded vacuum-cast No. 1	NaK	...	800, max 900	49 hr	10 ft/sec	.63	0.986
Extruded vacuum-cast No. 2	NaK	...	800, max 900	49 hr	10 ft/sec	.68	1.070
Vacuum-cast	NaK	...	800, max 900	49 hr	10 ft/sec	.62	0.978
Brush Premium QT	NaK	...	800, max 900	49 hr	10 ft/sec	1.00	1.651
Brush QT	Na	...	930	7-13 days	10 ft/sec	...	0.33
Brush Premium QT	Na	...	930	7-13 days	10 ft/sec33
Brush QT	Na (O free)	...	930	7 days	10 ft/sec34
Brush Premium QT	Na (O free)	...	930	13 days	10 ft/sec23
Extruded vacuum-cast	Na (O free)	...	930	30 days	10 ft/sec54
Extruded vacuum-cast	Na	Ni	930	Short time	Static	0.15	.238
Extruded vacuum-cast	Na	18-8	930	Short time	Static	.04	.554
Extruded vacuum-cast	Na	Be	930	Short time	Static	.06	.138
Brush QT	Na	347 Stainless	930	3 mo	Static	.16	...
Pressed Premium Grade	Na	347 Stainless	930	3 mo	Static	.15	...
Pressed vacuum melted	Na	347 Stainless	930	3 mo	Static	.10	...
Pressed Technical Grade	Na	347 Stainless	930	3 mo	Static	.12	...
Pressed Premium No. 1	Na (Ca treated)	347 Stainless	930	7 days	Static	.01	0.018
Pressed Premium No. 2	Na (Ca treated)	347 Stainless	930	7 days	Static	.02	.024
Pressed Premium No. 3	Na (Ca treated)	347 Stainless	930	7 days	Static	.01	.018
Pressed Technical	Na (Ca treated)	347 Stainless	930	7 days	Static	.05	.06
Extruded	Na (+0.1% Ca)	347 Stainless	930	1 mo	Static	.05	...
Extruded	Na (+2.0% Ca)	347 Stainless	930	4 mo	Static	< .01	...

OTHER

After 24 hr in molten sodium hydroxide at 1000°F, beryllium showed pitting and exfoliation.

PROTECTIVE TECHNIQUES

PLATING (ELECTROCLADDING)

In order to obtain an adherent, electroplated deposit on beryllium, it is necessary to pretreat the beryllium surface. The following two methods have been used with considerable success:

A. Direct method

1. Clean (vapor degrease, alkaline clean, etc.)
2. Anodic pickle
 - 10 vol % phosphoric acid (85-% H_3PO_4)
 - 2 vol % hydrochloric acid (38-% HCl)
 - Balance water
 - $80 \pm 10^\circ\text{F}$, 150 amp/sq ft, 2 min
3. Chemical pickle
 - Concentrated nitric acid (70-% HNO_3)
 - $80 \pm 10^\circ\text{F}$, 2 min
4. Water rinse
5. Chemical pickle
 - 100 gm/l $(\text{NH}_4)_2\text{SO}_4$
 - pH 2.0 with H_2SO_4
6. Water rinse
7. Plate with copper, nickel, zinc, tin, silver, or iron from solutions suitable for plating on an active metal, e.g. zinc.

B. Zinc-immersion method

1. Clean (vapor degrease, alkaline clean, etc.)
2. Immersion coat with zinc
 - $\text{Na}_4\text{P}_2\text{O}_7$ 120 gm/l
 - $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 40 gm/l
 - KF 10 gm/l
 - K_2CO_3 5 gm/l
 - pH 7-8 with H_2SO_4 and H_3PO_4
 - $180+^\circ\text{F}$, 3- to 5-min immersion
3. Water rinse
4. Copper plate on zinc, 0.1 to 0.4 mils
5. Water rinse
6. Plate other metals on copper base

CLADDING

The roll or diffusion cladding of beryllium is difficult because of its tendency to form brittle phases with the various cladding metals at elevated temperatures. Generally, attempts to roll clad beryllium have been only partially successful because of brittle interface formations between the two materials. During rolling and cooling, these brittle phases frequently are fractured. It is advisable to lessen the rate of the intermetallic-diffusion layer formation in roll cladding by using heavy reductions and keeping the time at elevated temperatures to a minimum. Attempts to roll clad QMV beryllium with nickel, Armco iron, Monel, titanium, zirconium, Inconel, and Type 304 Stainless were unsuccessful because of weak bonds. Copper, silver, molybdenum, tungsten, niobium, tantalum, manganese, chromium, cobalt, platinum, and palladium diffusion couples with beryllium formed brittle interfaces.

METALLOGRAPHY

The specimen is carefully ground on a dry or kerosene-lubricated silicon carbide disc. Usually, only the 240- and 400-grit discs are required, and they should be sharp. The polishing may be carried out on a small 1750-rev/min wheel covered with worsted serge using an etch-polish mixture of 10 percent oxalic acid and levigated alumina or rouge. An

alternate method, reported to be better from the standpoint of reproducibility and preservation of the constituents, is to polish with a slurry of cp MgO in 30-percent hydrogen peroxide on a billiard cloth-covered wheel. An etchant of a 1 to 9 mixture of 48-percent hydrofluoric acid and 190-proof ethyl alcohol has been found satisfactory. Another recommended etchant is 2 percent hydrofluoric acid in water.

An electropolishing and electroetching technique has been used in which the specimen is polished directly from 400-grit paper in 60 sec. The polishing solution consists of 900 ml H_3PO_4 , 240 gm Cr_2O_3 , and 200 ml H_2O . The specimen should not be mounted in bakelite. Using a lead cathode and 23 v, the polishing is carried out at 70°-80°C. The electro-etching is done at room temperature in fuming nitric acid employing 18 v, a stainless-steel cathode, and an etching time of 20-40 sec.

Polarized light is effective in bringing out grain boundaries. Tucker's reagent has been used for the determination of grain size. Inspection for cracks can be facilitated by etching the polished surfaces with 5 percent H_2SO_4 in water.

CONSTITUTIONAL DIAGRAMS

The constitutional diagrams for the principal binary alloys are available in the references indicated in Table 1.4.18.

Table 1.4.19 gives data regarding some of the constitutional features of various beryllium alloy systems.

Table 1.4.20 illustrates the effect of alloying additions on the tensile strength of beryllium.

Table 1.4.18—A List of the Principal Constitutional Diagrams of Binary Beryllium Alloys

Binary System	Reference
Beryllium-aluminum	ASM Metals Handbook, 1948
Beryllium-copper	{ ASM Metals Handbook, 1948 CT-3439, MIT, Jan. 1946
Beryllium-iron	TID 67 - J. of Met. and Cer., Issue No. 3, May, 1949 (classified)
Beryllium-nickel	ASM Metals Handbook, 1948
Beryllium-silver	Auf der Zweistofflegierungen, 1936
Beryllium-silicon	Auf der Zweistofflegierungen, 1936
Beryllium-uranium	Chapter 1.22, "Uranium and Its Alloys"
Beryllium-zirconium (Hypothetical Diagram,	SEP 13 - Sylvania Electric Products H. H. Hausner and H. S. Kalish, Secret, March 28, 1949 (classified)

Table 1.4.19—Data for Beryllium Alloy Systems

Element	Solid solubility in Be		Eutectic		Constituents	Remarks
	Temp., °F	Wt. %	Temp., °F	Wt. %		
Aluminum		1	1195	0.9 Al		
Bismuth		0.1				Liquid immiscibility indicated
Boron		Small				
Boron			2060	10–20		
Calcium		Small				Compound 26.7% Ca
Carbon		Small				Compound Be ₂ C
Cerium		Small				
Chromium		Small				
Cobalt	1965	10–15				
Copper	930	20	2100	61 Cu		
Copper	2060	36	~1600	~93 Cu		
Germanium		Small				
Gold		Small	930–1020			Compound AuBe ₅
Iron	2250	~2.5	2235	23 Fe		
Iron			2130	92 Fe		
Magnesium		Small				Distills from Be at 1650°F
Mercury		Very low				Insoluble
Molybdenum						Compounds (MoBe ₂) ₄ and (MoBe ₁₃) ₄
Nickel	2265	~10				3 eutectics between 2114° and 2264°F
Niobium		Small				
Osmium		Small				
Oxygen		Fairly high				
Palladium	1110	8				
Palladium	2100	24				
Platinum		Small				
Rhodium		Small				
Ruthenium		Small				
Selenium		Small				
Silicon			1995	61 Si		
Silver	1920	8–10	1620	~98 (?)		
Sulfur		Small				
Thorium		Small				
Tin		0.1		Close to tin end		Liquid immiscibility
Titanium		Small				Compound Ti Be ₁₂
Uranium			1940		U + UBe ₁₃	
Uranium			2190–2280		Be + UBe ₁₃	
Uranium	2100	Small				
Zirconium		Small				

Table 1.4.20 — The Effect of Alloying Elements on the Tensile Properties of Beryllium
(Kaufmann, Gordon, and Lillie, ASM Trans 1950; p 840)

Added element, %	Extrusion temp., °F	Anneal		Breaking stress,* lb/sq in.	Elongation, %
		Temp., °F	Time, hr		
0.73 Ti	1400	As extruded		43,200	0.42
.73 Ti	1400	1340	20	53,700	1.6
.73 Ti	1400	1340	20	53,600	1.1
.73 Ti	1400	1340	20	32,900	0.15
.73 Ti	1400	1380	5	51,400	1.2
.65 Zr	1390	As extruded		37,200	0.2
.65 Zr	1390	1340	20	40,400	1.4
.65 Zr	1390	1340	20	48,400	2.2
.65 Zr	1390	1290	50	47,100	2.6
.05 Mg	1350	As extruded		40,400	0.19
.05 Mg	1350	1340	20	42,700	2.3
.05 Mg	1350	1340	20	42,300	2.4
.60 Ce	1380	As extruded		38,100	0.1
.60 Ce	1380	1340	20	40,400	0.18
.60 Ce	1380	1340	20	42,500	.15
.60 Ce	1380	1380	5	44,500	1.5
.60 Ce	1380	1470	5	37,600	1.0
1.45 Ca	1400	As extruded		40,000	0.29
1.45 Ca	1400	1340	20	49,400	1.4
1.45 Ca	1400	1340	20	51,100	1.3
1.45 Ca	1400	1340	20	37,600	0.68
1.45 Ca	1400	1380	5	52,800	2.7
0.05 S	1410	As extruded		53,100	0.17
.05 S	1410	1340	20	49,100	1.2
.05 S	1410	1340	20	38,600	0.45
.05 S	1410	1380	20	47,400	3.0
.05-.5 Se	1365	As extruded		46,700	0.44
.05-.5 Se	1365	1340	20	42,000	.44
.05-.5 Se	1365	1340	20	46,900	.26
.05-.5 Se	1365	1380	5	33,400	.86
.05-.5 Se	1365	1470	5	47,100	2.7
.62 Al	1265	As extruded		50,800	0.18
.62 Al	1265	1340	20	47,700	1.9
.62 Al	1265	1340	20	45,500	2.4
.62 Al	1265	1340	20	50,000	3.0
3.0 Al	1245	As extruded		56,600	0.57
3.0 Al	1245	1340	20	51,500	2.3
3.0 Al	1245	1340	20	47,200	2.7
15.0 Cu	...	As extruded		49,400	0.19
15.0 Cu	...	1470	5	51,900	.19
10.0 Ni	...	As extruded		57,300	.25
10.0 Ni	...	1470	5	60,600†	.23

*Ultimate tensile strength

†Broke in grips

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CHAPTER 1.5

Beryllium Carbide

J. F. Quirk

REACTOR APPLICATION

Beryllium carbide has potential value as a moderator in nuclear reactors. In addition to its high moderating efficiency and low cross section, it has refractory properties which appear to be of interest for high-temperature moderation of nuclear reactions.

ABUNDANCE AND AVAILABILITY

Present processes for the production of beryllium carbide involve the high-temperature reaction of beryllium metal or beryllium oxide with carbon or graphite. The availability of these materials in "reactor-grade" purity is described in Chap. 1.4, "Beryllium and Its Alloys," and in Chap. 1.9, "Graphite." Equipment required for the production of beryllium carbide consists of conventional heating equipment and chemical process equipment which does not limit the availability of the product.

Beryllium carbide has been produced for experimental use only. In 1950, less than 1000 lb of beryllium carbide, valued at about \$100/lb, was produced.

EXTRACTION AND PURIFICATION

SYNTHESIS REACTION

Beryllium carbide may be prepared by heating a mixture of beryllium metal or beryllium oxide with carbon. A finely ground, intimate mixture of beryllium metal powder and carbon may be reacted by heating at temperatures of about 1800°F or higher in a vacuum or in an inert gas such as argon.¹ The yield and structural characteristics of the Be_2C produced depend on such variables as the time and temperature of heat treatment, mass of charge, and reactant particle sizes, but, in general, reaction at 2500°F for 4 hr yields a microcrystalline, fluffy, gray-black powder, while reaction at 4000°F for 30 min gives a 90-percent yield of coarsely crystalline beryllium carbide which has an average crystal size of 65 microns.

The reaction of beryllium oxide with carbon produces beryllium carbide and carbon monoxide, and for finely ground reactant mixtures, the reaction occurs at appreciable rates at temperatures above about 2730°F. The yields for this reaction appear to be somewhat lower than for the beryllium-carbon reaction. For a typical heat, a 2-lb batch of a stoichiometric mixture of fluorescent-grade beryllia and graphite are ball-milled and charged into a graphite crucible which is then flushed with argon and heated by induction

¹References appear at end of chapter.

to a minimum temperature of 3450°F for 4 hr. The heat-treated material contains about 60 percent of beryllium carbide and 40 percent of unreacted beryllium oxide and graphite.

COMMERCIAL PRODUCTION

Beryllium carbide has been produced on a pilot-plant scale by the Fansteel Metallurgical Corporation. The methods employed involve the reaction of intimately mixed, stoichiometric amounts of BeO (refractory grade, fused) and lampblack. The mixed powder, which in some cases is compacted before heating, is charged into a graphite crucible and heated by induction while hydrogen flows through the charge. For a 5-lb charge, a maximum power input of 40 kw is used to raise the reaction temperature to 4080°F in about 1 hr. After maintaining this temperature for 2 hr during which time the evolution of CO is completed, the charge is cooled in an atmosphere of flowing hydrogen and contains, on the average, about 1½ lb of minus 80-mesh, crystalline beryllium carbide. This corresponds to a yield of about 75 percent. After brushing to remove a crucible reaction layer, the charge is tumbled in a ball mill and then screened and stored in sealed glass containers. Material made by this process has been used in most of the experimental processing and fabrication of beryllium carbide.

PHYSICAL AND CHEMICAL CONSTANTS

Some of the physical and chemical constants of beryllium carbide are given in Table 1.5.1.

CHEMICAL COMPOSITION

Pure beryllium carbide, Be₂C, contains 60 percent by weight of beryllium and 40 percent of carbon in chemical combination. Material made by the processes described above is usually associated with considerable amounts of graphite, beryllium oxide, beryllium hydroxide, and nitrogen, in addition to the minor impurities which may be introduced with the reactant materials. The range in chemical composition for 13 different lots of carbide which were made by Battelle Memorial Institute and the Fansteel Metallurgical Corporation is shown in Table 1.5.2.

CRYSTALLOGRAPHY

STRUCTURE

Beryllium carbide crystallizes in the isometric system and has a cubic antiferite type lattice with unit-cell dimension of about 4.344Å. The isotropic crystals have an index of refraction of 2.64 ± 0.02 as measured for the red (lithium) wave band in transmitted white light. Be₂C may be regarded as a salt of methane in which a close-packed structure is built of C⁴⁻ ions with the metallic cations between them.

CHARACTERISTICS

Beryllium carbide occurs in only one crystal system but in a variety of crystalline sizes and habits which range from the microcrystalline nodular, or "grape-cluster," aggregates formed in "low-temperature" material to the coarsely crystalline euhedral* grains which are formed in powder mixtures reacted at temperatures above about 1700°C. The color of

*Of well developed and characteristic form and symmetry.

Table 1.5.1 — Physical and Chemical Constants of Beryllium Carbide

Density, * gm/cm ³	2.44
Calculated from X-ray measurements	2.30–2.40
Crystals from BeO-C reaction	
Melting point	Beryllium carbide dissociates, with rapid vaporization of beryllium, when heated in argon at atmospheric pressure at a temperature of about 2150°C. It has no useful melting point at atmospheric pressure. When heated rapidly to temperatures above 2200°C, some melting is observed, but the rapid dissociation which occurs interferes with a conventional melting-point determination
Free energy of formation ($\Delta F^\circ_{2127^\circ\text{C}}$), kcal	-7.83
Specific heat† (30° to 100°C), cal/(gm)(°C)	
98% Be ₂	0.334 ± 0.013
Vapor pressure, ‡ atm	
1627°C	6×10^{-3}
1827°C	4×10^{-2}
2127°C	0.44
2327°C	1.5
Coefficient of linear thermal expansion, per °C	
25° to 50°C	5.6×10^{-6}
25° to 200°C	7.7×10^{-6}
25° to 400°C	9.5×10^{-6}
25° to 600°C	10.5×10^{-6}
Thermal conductivity, ² watts/(cm)(°C)§	$K(t) = 0.15 \times 10^{-4}t + 87 \times 10^{-4}$ (±200, 300°–950°C), where $t = ^\circ\text{C}$. For $t = 30^\circ\text{C}$, $K = 0.09$ watts/(cm)(°C)
Electrical properties	The electrical properties of pure Be ₂ C have not been reported. Impure carbide in the form of sintered shapes which were fabricated by Battelle had electrical resistivity values of 0.063 ohm-cm at 30°C and 0.047 ohm-cm at 425°C. Values reported by Draghic ³ for a hot-pressed specimen of Be ₂ C ranged from 1.09 ohm-cm at 65°C to 0.047 ohm-cm at 975°C. It was observed that the resistivity values varied greatly for samples containing different amounts of free carbon, and it is probable that pure beryllium carbide would have very high electrical resistivity. It was observed that the heating of beryllium carbide grains by induction at a frequency of 275 kc also varied greatly for samples containing different amounts of free carbon. Samples of relatively pure material were heated very slightly at this frequency

*Gm/cm³ × 62.43 = lb/cu ft

†Cal/(gm)(°C) × 1 = Btu/(lb)(°F)

‡In equilibrium with beryllium carbide

§Watts/(cm)(°C) × 0.239 = cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

Table 1.5.2—Range in Chemical Composition for Thirteen Lots of Beryllium Carbide

Compound	Typical	Analysis, wt-%	
		Lowest	Highest
Be ₂ C	91.30	87.5	98.0
BeO	1.89	0.1	3.8
Be(OH) ₂ *	1.02	.1	3.6
N ₂ †	3.13	1.2	5.5
Free C	2.66	1.0	5.3

*Hydrogen, determined by analysis, was assumed to be present as Be(OH)₂

†Nitrogen may have been present in solid solution or as the compound Be₃N₂

the crystals varies from translucent yellow through orange, dark red, and brown, to metallic gray-black and is probably influenced primarily by the amount and dispersion of free carbon in the crystals. Hydrolysis of the crystal surfaces causes the dark red color to appear pink.

Euhedral* Be₂C crystals occur commonly as octahedrons, dodecahedrons, and tetrahedrons, and they exhibit octahedral cleavage in four directions. Twinning, which was commonly observed in the high-temperature product, occurred as twolings, threelings, and in the form of a chain-like structure containing up to 25 crystals which were usually joined at 45-degree angles. Contact twin crystals of the Carlsbad type occurred commonly.

Be₂C which has been heated at temperatures above about 2260°C usually contains graphite flakes, precipitated as a decomposition product, either on the crystal surfaces or within the crystals. Precipitated flake graphite is especially abundant in Be₂C which has been heated to incipient fusion.

Beryllium carbide crystals which are heated at about 2100°C in nitrogen dissolve various amounts of the gas with an accompanying change in cell dimensions of 0.004A for each weight-percent of nitrogen dissolved.

HEALTH HAZARDS

The toxicity of beryllium carbide is not known precisely, but it is assumed to be of the same order as that of beryllium oxide. The same health precautions are therefore recommended.

HANDLING AND STORAGE

Hydrolysis of beryllium carbide results in a large volume increase owing to the formation of low-density beryllium hydroxide. For this reason, it is necessary to store and process the material in a moisture-free atmosphere. Because of the health hazard involved, beryllium carbide, especially in the form of finely ground powder, should not be stored in glass or other brittle containers which might be broken by the expansion of the carbide.

*Of well developed and characteristic form and symmetry.

MECHANICAL PROPERTIES

MODULUS OF RUPTURE

Sintered compacts of beryllium carbide have average moduli of rupture values of 8,000 to 10,000 lb/sq in. when tested at room temperature and values of 7,000 to 14,000 lb/sq in. when tested at 2500°F. These values, which are for $\frac{1}{4}$ -in. \times $\frac{1}{4}$ -in. \times 3-in. compacts with porosities of 5 to 35 percent, appear to be influenced primarily by the nature of the intergranular material in the compacts. Compacts which contain intergranular graphite, formed by decomposition during the sintering heat treatment, have reduced strengths.

MODULUS OF ELASTICITY

Modulus of elasticity values determined for sintered beryllium carbide compacts by a static-load method range from 30×10^6 to 35×10^6 lb/sq in. These values are for test specimens 3 to 5 in. long of $\frac{1}{4}$ -in.-square cross section with apparent porosities of 10 to 25 percent. Modulus of elasticity values for a similar bar, tested by a dynamic method at various temperatures, are shown in Fig. 1.5.1.

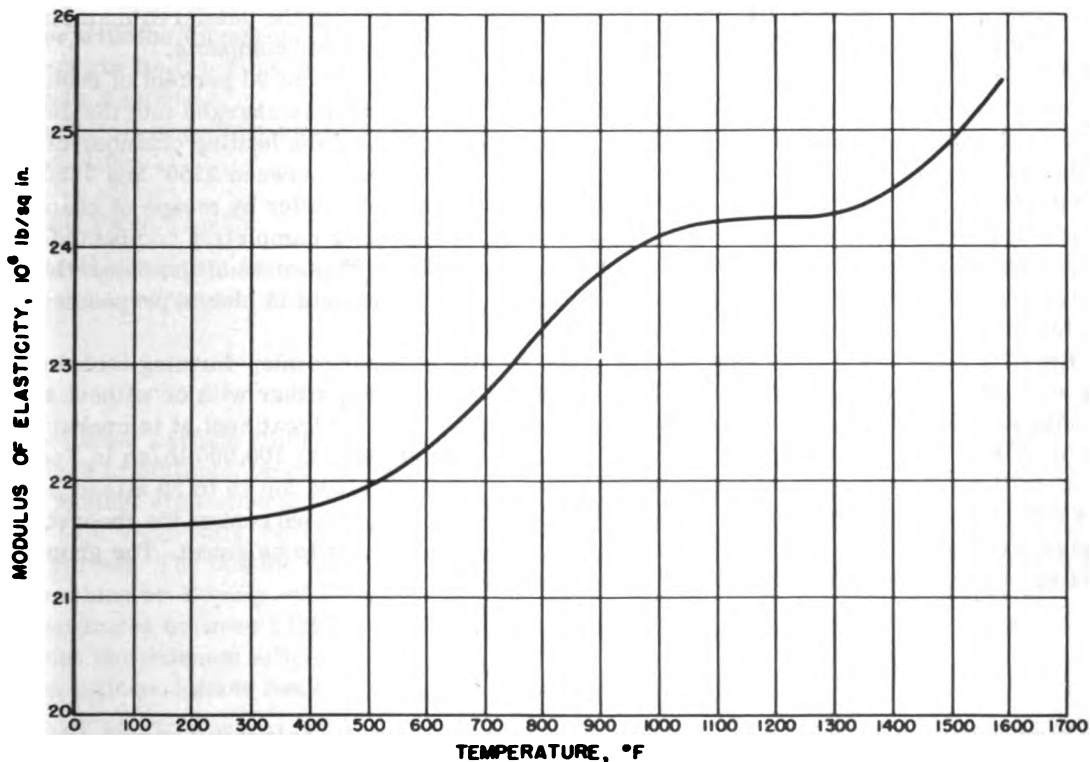


Fig. 1.5.1—Dynamic Modulus of Elasticity of Sintered Beryllium Carbide with Temperature. Reprinted from Report for the Month of June, 1950, Battelle Memorial Institute, June 16, 1950.

Figure 1.5.1 indicates that the modulus of elasticity for this specimen is somewhat higher at 1600°F than at room temperature. This result, together with an indicated increase in transverse strength at high temperature, is thought to be a significant property of the intergranular bonding phase.

HARDNESS

Measurements for euhedral Be_2C crystals mounted in lucite and measured with a Tukon hardness tester give an average Knoop hardness of 2550 for a 50-gm load and a value of 2740 for a 25-gm load. The hardness is greater than that of silicon carbide and somewhat less than that of boron carbide.

THERMAL-SHOCK RESISTANCE

Limited test results indicate that the thermal-shock resistance of compacted beryllium carbide is low compared with other ceramics. Plate-and-spacer assemblies⁴ which were constructed with hot-pressed Be_2C -graphite shapes failed by cracking when cooled from 2000°F to room temperature in $1\frac{1}{2}$ hr or when cycled four times between 2000°F and 1475°F.

Thermal-throughput tests also indicated that individual compacts have low resistance to thermal-stress cracking.⁵

FORMING AND FABRICATION

Beryllium carbide-base bodies may be formed by hot-pressing the powdered material or by pressing at room temperature and then sintering the powder compacts.

For a typical hot-press fabrication procedure, a mixture of about 90 percent of minus 80-mesh beryllium carbide powder and 10 percent of lamp black is charged into the cavity of a thick-walled graphite mold; the filled mold is inserted into the heating chamber of an induction furnace and then heated by induction to a temperature between 3350° and 3550°F. Pressure of about 3000 lb/sq in. is then applied to the heated powder by means of graphite rams and is maintained for 20 min or longer until the charge is completely compacted. Small compacts made in this manner have densities of 90 to 95 percent of the theoretical value and are generally sound but show some tendency to laminate in planes perpendicular to the pressing direction.

Beryllium carbide shapes may be fabricated by conventional powder-forming techniques in which finely ground beryllium carbide powder is compacted, either with or without a binder addition, at room temperature and then hardened by heat treatment at temperatures of 3600° to 4200°F. Compacts which are hydrostatically pressed at 100,000 lb/sq in., packed in beryllium oxide powder in graphite capsules, and then sintered for 15 to 30 min at about 3900°F in a flowing argon atmosphere, have densities of 75 to 90 percent of the theoretical value, are relatively free of decomposition graphite, and appear to be sound. The properties of such shapes are similar to those noted above.

HEAT TREATMENT

Beryllium carbide powder compacts gain strength and rigidity by crystal growth or recrystallization which occurs during heat treatment. The rate of recrystallization appears to increase with increases in sintering temperatures, which are limited in practice by the decomposition of Be_2C . This decomposition which causes the deposition of intergranular graphite is inhibited to some extent by the presence of beryllium oxide surrounding the powder compact during heat treatment. Under these conditions, the deposition of beryllium oxide, possibly from the vapor phase, in the pores of the powder compact results in an apparent density increase during sintering. Beryllium carbide powder compacts ordinarily do not increase in bulk density during sintering when heated in an inert gas at atmospheric pressure.

MACHINING

Sintered beryllium carbide shapes may be formed by grinding, preferably with a diamond abrasive, using a nonaqueous liquid such as carbon tetrachloride or kerosene as coolant.

CORROSION BEHAVIOR

ATMOSPHERIC

Beryllium carbide is very reactive. It is attacked by water or water vapor at room temperatures and by oxygen or nitrogen at elevated temperatures. The rate of reaction with water vapor ($\text{Be}_2\text{C} + 4\text{H}_2\text{O} \rightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4$) is illustrated by Figs. 1.5.2 and 1.5.3. Figure 1.5.2 shows the water absorption for Be_2C powders which were exposed to various air-water vapor mixtures at 77°F. Figure 1.5.3 shows the rates of reaction of sintered Be_2C compacts which were exposed at 400°F to air which was saturated with water vapor at 70°F. Attack by water vapor is accompanied by a large increase in the bulk volume of beryllium carbide grains or compacts.

Beryllium carbide reacts with nitrogen or oxygen at elevated temperatures. Mallett and Thomas⁶ reported that the reaction with nitrogen occurs at a temperature of 1830°F or higher with the formation of Be_3N_2 and free carbon and that a limiting equilibrium ratio of Be_3N_2 to Be_2C occurs at about 2000°F. Above 2000°F the reaction is reversed and Be_3N_2 tends to dissociate.

The effect of density on the oxidation of hot pressed Be_2C rods heated in dry air is shown in Fig. 1.5.4.

OTHER REACTANTS

Attack on beryllium carbide by a number of chemical reagents is illustrated by the qualitative data of Table 1.5.3.

PROTECTIVE TECHNIQUES

Beryllium carbide compacts have been coated with protective metal or ceramic films. Coatings of platinum or of siliceous ceramic glazes are reported to provide good resistance against atmospheric attack at temperatures up to 2500°F. These coatings were applied to low-porosity, hot-pressed specimens of Be_2C which contained 12 to 35 percent of free carbon. The coating materials were applied in the form of organic-liquid suspensions by brushing or dipping and then maturing by heating in normal or inert atmospheres at temperatures between 2700° and 3500°F. A coating of 20-percent siliceous glass and 80-percent molybdenum silicide (MoSi_2) is reported to provide good protection.

The siliceous glass has the following composition:

SrO	- 0.28 mole,
Li_2O	- 0.64 mole,
SiO_2	- 1.01 mole.

The glass-molybdenum silicide coating was matured by heating in air for 30 min at 2700°F. In general, the coatings were thought to protect the underbody by promoting the formation of a tightly-adherent, beryllia-rich covering layer which retarded further reaction.

Attempts to apply refractory protection coatings to beryllium carbide by vapor deposition techniques have not been successful.

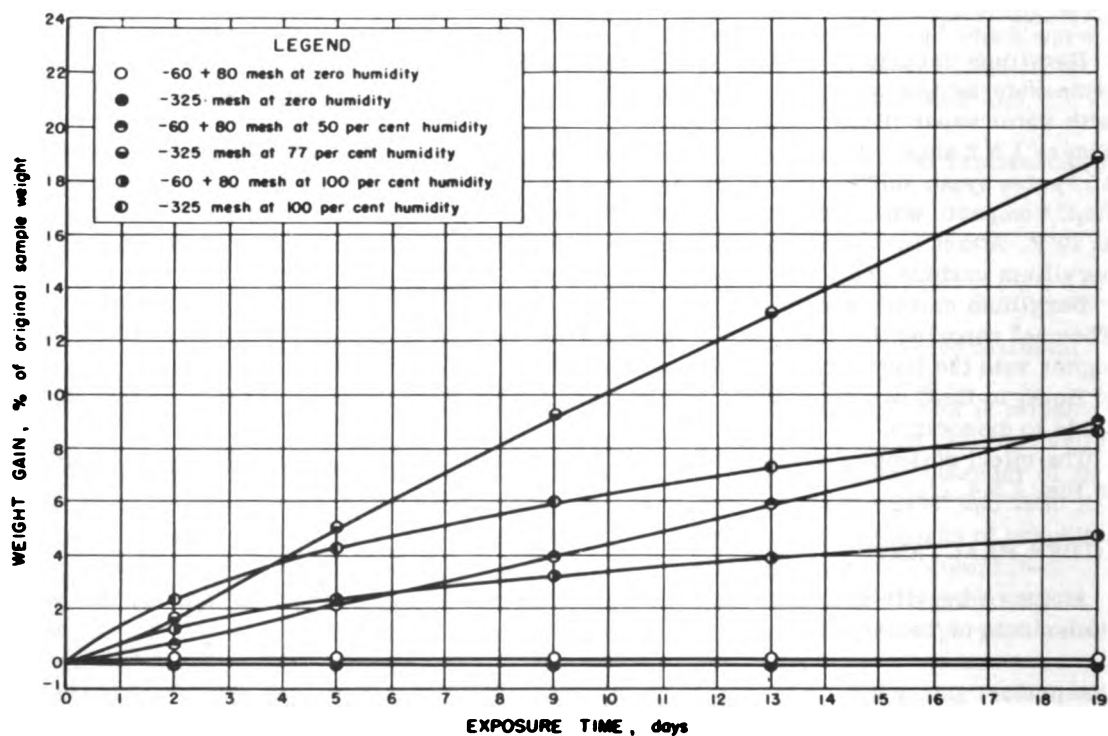


Fig. 1.5.2—Weight Gain of Beryllium Carbide Powder After Exposure to Moist Air at 77°F. Reprinted from C. G. Harman and L. S. O'Bannon, BMI-712, Apr. 30, 1951.

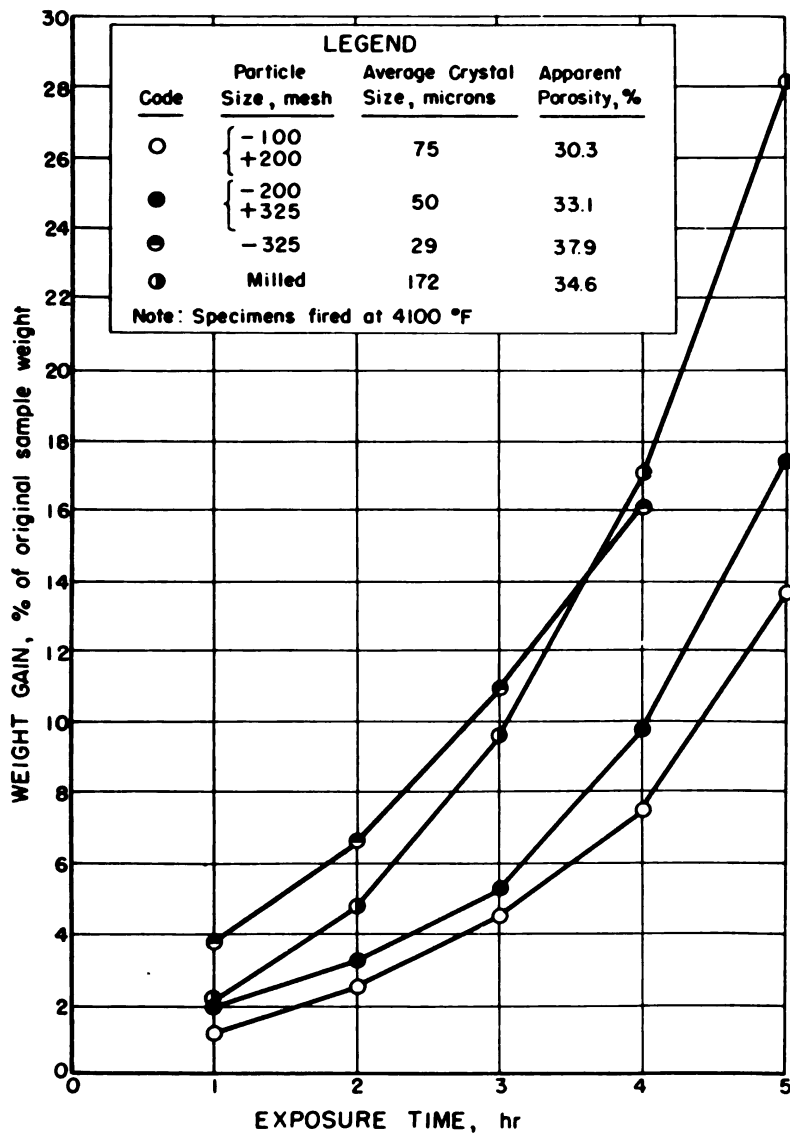


Fig. 1.5.3—Weight Gain in Moist Air at 400°F of Beryllium Carbide Compacts Prepared from Various Grain Sizes. Reprinted from C. G. Harman and L. S. O'Bannon, BMI-712, Apr. 30, 1951.

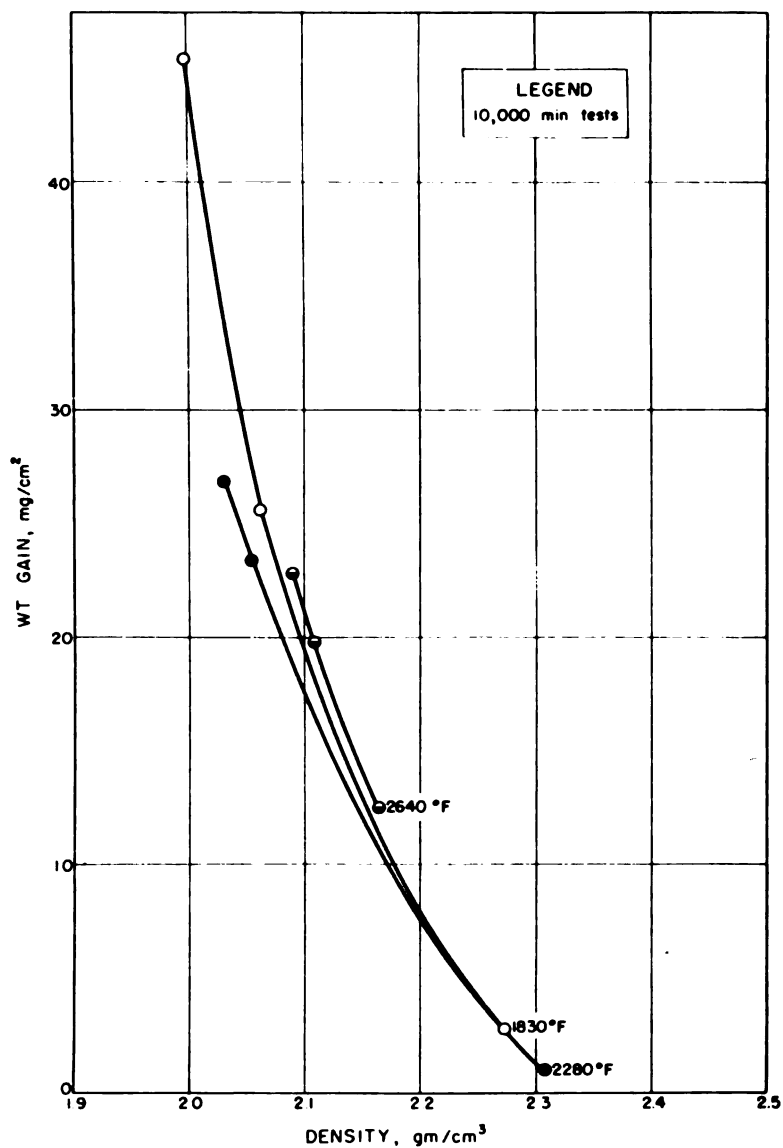


Fig. 1.5.4—Effect of Density on Oxidation of Pressed Be_2C Rods. Reprinted from C. G. Collins and J. W. Sausville, Report of the Investigation of the Stability of Be_2C in Moist and Dry Air, July 22, 1948.

Table 1.5.3—Summary of Lebeau's Data on the Reaction of Be_2C With Various Reagents
(P. J. Lebeau, J. Phys. Chem., Vol 4, 1899)

Reactant	Temperature, °F	Principal reaction products
F_2	Heated	$\text{BeF}_2 + \text{C}$
Cl_2	Heated	$\text{BeCl}_2 + \text{C}$
Br_2	Heated	$\text{BeBr}_2 + \text{C}$
I_2	1470	No reaction
O_2	Heated	Superficial attack
S	1830	BeS
HF	840	BeF_2
HCl	1110	$\text{BeCl}_2 + \text{C} + \text{H}_2$
HI	1380	$\text{BeI}_2 + \text{CH}_4$
H_2O	...(Slowly)	$\text{Be}(\text{OH})_2 + \text{CH}_4$ (pure)
KOH (soln)	...(Rapidly)	$\text{Be}(\text{OH})_2 + \text{CH}_4$
H_2SO_4 (conc)	...	Reduces
HNO_3 (conc)	...	Slowly reduces
HCl (conc)	...	Slowly reduces
HNO_3 (dil)	...	Complete soln in few hr
HCl (dil)	...	Complete soln in few hr
KOH (fused)	Incandescence	Attacks
KMnO_4	...	Oxidizes
PbO_2	...	Oxidizes
KClO_3	...	No reaction
KNO_3	...	No reaction
Na^*	932	+ 4.5 mg/(cm ²)(mo); specimen swelled due to hydration after test

*Communication from J. P. Howe, General Electric Research Laboratory, Schenectady,
N. Y. Oct. 20, 1952

Table 1.5.4—Glaze Compositions Which Appear Promising From Oxidation Tests
at 200° to 2500°F

Constituent oxides	Composition, wt-%	
	Glaze No. 149	Glaze C
Na_2O	13.2	4.43
Li_2O	5.7	1.73
SrO	...	16.37
BaO	3.5	...
TiO_2	8.6	...
Al_2O_3	6.3	11.75
SiO_2	62.8	51.60

Siliceous ceramic coatings have been reported which provide good protection for hot-pressed beryllium carbide compacts which contained 12 to 35 percent free carbon. Typical promising glaze compositions in oxidation tests at 200° to 2500°F are shown in Table 1.5.4.

These glazes were applied to compacts which had been preoxidized by heating for 2 to 5 min in air at temperatures between 1700° and 2200°F. The coatings were matured by heating in air at temperatures between 2700° and 3100°F.

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CHAPTER 1.6

Bismuth

M. C. Udy

REACTOR APPLICATION

Since bismuth is a metal with relatively low melting point and a low-absorption cross section for thermal neutrons, it has possibilities for use as a liquid fuel-carrying medium in nuclear reactors or as a liquid-metal coolant. It might possibly find application as a constituent of low-melting liquid-metal control mediums in which the high cross section would be supplied by some other element.

ABUNDANCE AND AVAILABILITY

Bismuth is estimated to exist in the earth's crust to the extent of about 0.00002 percent. The most common bismuth minerals are native bismuth, bismuthinite (Bi_2S_3), bismite ($\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), and bismutite ($\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$). Sorting of the bismuthinite ore at the Tasna mine in Bolivia yields material containing more than 25 percent bismuth. Bismuth is also found as a lower grade material in the tin deposits of Bolivia, in the bismuth-cobalt deposits of Saxony, and in the bismuth-gold deposits of Australia and the United States.

Estimated world bismuth production for 1949 is 1,500,000 lb. The May 1952 price for bismuth was \$2.25 per pound in ton lots.

EXTRACTION AND PURIFICATION

Bismuth is extracted from rich ores by smelting in a reverberatory furnace. Iron is added to decompose any bismuth sulfide present, and lime, soda ash, salt cake, fluorspar, and feldspar are added as fluxes. Products are crude metallic bismuth, matte, speiss, and slag. The matte and speiss are crushed, roasted, and resmelted to recover their bismuth content.

When bismuth occurs in smelter by-products, a wet recovery method may be used. The finely divided, oxidized material, containing 5 to 20 percent bismuth, is treated with HCl. The solution from this treatment is further diluted, and bismuth oxychloride is precipitated. Lead chloride is removed from the precipitate by repeated hot-water leachings. The oxychloride is filtered, dried, and smelted with lime and charcoal to metallic bismuth.

The anode slime from electrolytic lead processes contains gold, silver, bismuth, and other metals of commercial importance. The slime is smelted, and lead, antimony, and arsenic are removed from the gold, silver, copper, tellurium, and bismuth by careful

oxidation. This slag is separated, and further oxidation removes the bismuth, copper, and tellurium and leaves a gold-silver doré bullion. The bismuth-containing slag is crushed to a small size, mixed with salt cake and coke breeze, and smelted in a small reverberatory furnace. Crude metallic bismuth, matte, and slag result. The matte and slag are reworked to recover their metallic values.

No difficulty is experienced in producing 99.95 percent pure bismuth.

Table 1.6.1 gives a typical analysis of the impurities in high-purity bismuth.

Table 1.6.1 — Typical Analysis of High-purity Bismuth

Element	Concentration, ppm
Fe	10
Ag	0.2
Cu	3.0
As	<1.0
Sb	<15.0
Pb	50
Si	100
Mg	10
Cr	10
Al	10

PHYSICAL AND CHEMICAL CONSTANTS

Selected physical and chemical constants of bismuth are given in Table 1.6.2.

MECHANICAL PROPERTIES

The mechanical properties of bismuth are given in Table 1.6.3.

MELTING AND CASTING

Bismuth can be melted satisfactorily in graphite or clay-graphite crucibles, although iron pots are preferred. It can be cast in chill molds.

Since bismuth expands 3.44 percent during solidification, castings do not contain the usual shrinkage pipe found in most metal castings. On the contrary, during normal cooling the top and sides of the casting solidify, and the excess metal resulting from expansion is exuded through the top. Sound, smooth-topped castings can be made by controlled cooling or by using a combination cap and riser to control the flow of excess metal.

Precision castings can also be made by die-casting methods.

FORMING AND FABRICATION

Forming and fabrication of bismuth are difficult because of its brittleness. However, bismuth can be extruded at temperatures close to the melting point.

HEAT TREATMENT

Bismuth can be completely annealed at 260°F.

Table 1.6.2—Physical and Chemical Constants of Bismuth

Thermal-neutron absorption cross section, barns/atom	0.032 ± 0.003	
Density, * gm/cm ³		
20°C (solid)	9.80	
271°C (solid)	9.74	
271°C (liquid)	10.07	
600°C (liquid)	9.66	
Melting point, °C	271	
Boiling point, °C	1627	
Heat of fusion, cal/mole	2510	
Heat of vaporization, cal/mole		
25°C	49,000	
1627°C	42,600	
Vapor pressure, atm		
600°C	10 ⁻⁶	
917°C	10 ⁻³	
1315°C	10 ⁻¹	
1627°C	1	
Heat capacity, † cal/(mole)(°C)		
25°C	6.10	
25 – 271°C	4.49 + 5.40 × 10 ⁻³ T	
271 – 1027°C	7.5	
25 – 1727°C (Bi ₂ gas)	8.94 – 0.10 × 10 ⁻⁵ T ²	
Enthalpy † (H _T – H _{25°C}), cal/mole		
Solid, 25 – 271°C	4.49T + 2.70 × 10 ⁻³ T ² – 1579	
Liquid, 271 – 1027°C	7.50T + 50	
Bi ₂ gas, 25 – 1727°C	8.94T + 0.10 × 10 ⁻⁵ T ² – 2699	
Entropy, 25°C., cal/(mole)(°C)		
Solid	13.6 ± 0.61	
Bi gas	44.68 ± 0.01	
Bi ₂ gas	65.4 ± 0.2	
Entropy (S _T – S ₂₅), cal/(mole)(°C)		
Temp., °C	Solid, Liquid	Bi ₂ gas
127	1.87	2.60
327	9.30	6.22
527	11.45	8.78
727	13.13	10.77
927	14.49	12.40
1727	...	16.96
Resistivity, μohm-cm		
-100°C	75.6	
0°C	106.80	
100°C	160.2	
300°C (liquid)	128.9	
500°C	139.9	
700°C	150.8	
Thermal expansion coefficient, per °C		
-185 – 15°C	13.0 × 10 ⁻⁶	
20 – 100°C	13.4 × 10 ⁻⁶	
Thermal conductivity, ‡ cal/(sec)(cm)(°C)		
18°C	0.0194	
89°C	.0181	
256°C	.0183	
286°C (liquid)	.0400	
700°C	.0368	
Crystallography	Rhombohedral; a ₀ = 4.7457 Å	
* gm/cm ³ × 62.43 = lb/cu ft		
† T = °K		
‡ cal/(sec)(cm)(°C) × (2.419 × 10 ³) = Btu/(hr)(ft)(°F)		

Table 1.6.3—Mechanical Properties of Bismuth

Modulus of elasticity, lb/sq in.	4.6×10^4
Shear modulus, lb/sq in.	1.8×10^4
Poisson's ratio	0.33
Hardness, Brinell	4–8
Impact strength (unnotched Charpy), ft-lb	
64°F	0.097
150°F	.147
200°F	.294
300°F	.514
400°F	.441
450°F	.441
Creep, lb/sq in., load for deflection rate of 0.001 in./ (in.) (hr)	
150°F	600
250°F	450
350°F	350
400°F	300

CORROSION BEHAVIOR

Bismuth is not readily attacked by air at ordinary temperatures but oxidizes at higher temperatures. Molten bismuth burns in air with a faint bluish-white flame. Bismuth does not react with nitrogen or hydrogen.

Bismuth reacts slowly with cold water and, at red heat, slowly decomposes steam. Bismuth is insoluble in cold H_2SO_4 but dissolves readily in hot concentrated acid. It dissolves in HCl only in the presence of oxygen. It reacts readily with HNO_3 .

Bismuth unites directly with chlorine, bromine, iodine, and sulfur.

Ferritic iron and plain steel have good resistance to attack by molten bismuth up to their transition temperatures, about 1290°F.

Resistance of other metals to attack by bismuth is shown in Table 1.6.4.

Bismuth of ordinary purity can be held for several days in quartz containers in the range 930 to 1830°F, but the bismuth tends to wet the quartz and even the wall coating may break it by expansion on freezing.

Vycor glass is a satisfactory container for bismuth at temperatures up to 1650°F.

Graphite crucibles last for several days when used with bismuth at temperatures up to 1830°F and exposed to the atmosphere. The graphite may crack if the bismuth freezes.

Silicon steel (transformer grade) appears, from preliminary data, to be a satisfactory container for bismuth at temperatures up to 1550°F.

CONSTITUTIONAL DIAGRAMS

Constitutional diagrams of the following elements with bismuth are discussed in the ASM "Metals Handbook":¹ aluminum, gold, cadmium, copper, iron, mercury, magnesium, lead, and tin. References to systems of bismuth with the following additional elements are given by Haughton:² silver, arsenic, boron, barium, carbon, calcium, cerium, cobalt, chromium, gallium, germanium, iridium, potassium, lithium, manganese, sodium, nickel, palladium, polonium, platinum, rhodium, sulfur, antimony, selenium, silicon, tellurium, thallium, and zinc.

¹References appear at end of chapter.

Table 1.6.4—Resistance of Metals to Attack by Bismuth

Metal	Remarks
Molybdenum	Good resistance to at least 2030°F
Chromium	Good resistance to 1350°F, limited resistance to 2030°F
Beryllium	Good resistance to 930°F and probably to 1830°F
Niobium	Good resistance to 900°F, limited resistance to 1350 to 2030°F
Aluminum	Good resistance at 570°F, poor at 930°F
Nickel and nickel alloys	Poor resistance above 520°F
Copper	Eutectic at 519°F, solubility 0.2
Manganese	Eutectic at 514°F, solubility 0.6
Magnesium	Eutectic at 500°F, solubility 0.54
Zinc	Eutectic at 490°F, solubility 2.7
Platinum	Eutectic at 511°F, solubility 1.0
Tin	Eutectic at 282°F, solubility 42.0

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CHAPTER 1.7

Carbides

M. W. Mallett and V. M. Shepline

Carbides may be of use as refractories, fuels, radiation shields, or structural materials. Probably their most important properties are high hardness and good thermal stability. Carbides of the transition elements are among the hardest and most refractory materials known and are chemically inert at ordinary temperatures. Some of the carbides, particularly those of the rare-earth elements, are good conductors of electricity. Titanium carbide is outstanding for its thermal-shock resistance and high tensile strength at elevated temperatures.

PHYSICAL AND CHEMICAL CONSTANTS AND PREPARATION OF METAL CARBIDES

Tables 1.7.1, 1.7.2, and 1.7.3 list the principal physical and chemical constants, the method of preparation, and the stability of metal carbides. All data are for the pure carbides only.

Table 1.7.4 lists selected properties of the common carbides.

Various crystal modifications are given for three alkaline-earth metal carbides, namely BaC_2 , CaC_2 , and SrC_2 . It is reported that polymorphism probably occurs in other carbides MC_2 of the calcium carbide type. $\alpha\text{-SiC}$ also has several crystalline forms, differing only in the arrangement of layers of atoms. Each type is designated by the number of layers in the unit cell, followed by the letter "H" or "R," depending upon whether the unit cell is hexagonal or rhombohedral. The Roman numerals were used in the old system of naming SiC forms and merely indicate the order of their discovery. For better comparison, lattice constants refer to a hexagonal unit cell.

Table 1.7.1—Physical and Chemical Constants of Some Metal Carbides

Carbide	Color	Density,* gm/cm ³	Melting point, °C	Boiling point, °C	Moh hardness	Solubility
Aluminum Al ₄ C ₃	Yellow	2.99†	>2800			Sol in acid; insol in acetone
Barium BaC ₂ (I) BaC ₂	Colorless	3.91† 3.81†	>1780			Sol in dil acid
Beryllium Be ₃ C	Translucent, amber	2.44	Decomposes at 2150		+9	Sl. sol in dil HCl, HNO ₃ at room temp.
Boron B ₄ C	Black	2.519	2350–2500	>3500	9.32	Insol in water, acid
Calcium CaC ₂ (I) CaC ₂ (II) CaC ₂ (III) CaC ₂ (IV)	Colorless	2.22† 2.04†	 2800			Sol in HCl
Cerium CeC ₂	Red	5.23				Sol in acid
Chromium Cr ₂₃ C ₆ Cr ₇ C ₃ Cr ₃ C ₂	 Silver Gray	 6.97 6.92 6.68	 1550 1665 1880	 3800	 +7	 Insol in aqua regia Insol in aqua regia Insol in water; sol in HCl
Cobalt Co ₅ C Co ₂ C	 Metallic gray	 8.07†				
Copper Cu ₂ C ₂ CuC ₂						
Hafnium HfC	Metallic gray	12.20	3887			
Iron Fe ₃ C Fe ₃ C Hägg Fe ₃ C Hägg	Gray	7.67 7.18†	1650		7–8	Insol in water; sol in dil acid
Lanthanum LaC ₂	Yellow	5.02				Insol in conc HNO ₃
Lithium Li ₂ C ₂	Colorless	1.68				Sol in acid
Magnesium Mg ₃ C ₃ MgC ₂	Gray Blue-black	2.21† 2.07†				
Manganese Mn ₂₂ C ₈ Mn ₇ C ₃ Mn ₃ C		7.49† 7.35† 6.89	1520			Sol in acid
Molybdenum Mo ₇ C MoC	White Gray	8.9 8.5	2687 2692		7–9 7–8	Insol in water; sol in HNO ₃ , HF
Neodymium NdC ₂	Yellow	5.15				Insol in conc HNO ₃ ; sol in dil acid
Nickel Ni ₃ C		7.957				

Table 1.7.1 — (Continued)

Carbide	Color	Density,* gm/cm ³	Melting point, °C	Boiling point, °C	Moh hardness	Solubility
Niobium						
NbC	Yellow-brown	7.82	3500			Insol in acid
Plutonium						
PuC		13.9†				
Pu ₂ C ₃		12.70				
Praseodymium						
PrC ₂	Yellow	5.10				Sol in dil acid
Samarium						
SmC ₂	Yellow	5.86				Sol in acid
Scandium						
ScC						
Silicon						
SiC (β)	Pale green to black	3.210	Decomposes at 2300		9.15	Insol in water, acid; sol in fused alkali
6H, SiC(II)(α)		3.208				
Silver						
Ag ₂ C ₂	White					Sol in AlClO ₄
Sodium						
Na ₂ C ₂	Colorless	1.575	Decomposes at 890			Sol in acid
Strontium						
SrC ₂ I	Black	3.27†	>1927			
SrC ₂ II						
SrC ₂		3.04†				
Tantalum						
Ta ₂ C		15.1†	3400			Sol in HF + HNO ₃
TaC	Metallic gold	14.48	3877		+9	Sol in HF + HNO ₃ ; insol in water, acid, alkali
Thorium						
ThC		10.65†	2625			
ThC ₂	Yellow	9.6	2655	5000		V. sl. sol in conc acid
Titanium						
TiC	Metallic gray	4.25	3140	4300	8–9	Sol in HNO ₃ ; insol in water, HCl
Tungsten						
W ₂ C (β)	Gray-green	17.20	2857	6000	9–10	Insol in water; sl. sol in HCl, hot HNO ₃
WC	Gray	15.50	2867	6000	+9	Insol in water, acid; sol in F ₂
Uranium						
UC	Metallic	13.63	2250			Insol in dil acid
U ₂ C ₃	Metallic	12.88†	2350–2400			Insol in acid
UC ₂	Metallic gray	11.28	2350–2400	4370	+7	
Vanadium						
VC	Silvery gray	5.36	2830	3900	9–10	Insol in water, HCl, H ₂ SO ₄ ; sol in HNO ₃
Yttrium						
YC ₂	Yellow	4.13				
Zirconium						
ZrC	Metallic gray	6.70	3530	5100	8–9	Insol in water; sol in HF, HNO ₃

*Gm/cm³ × 62.43 = lb/cu ft

†Calculated X-ray density

Table 1.7.2 — The Crystallography and Thermodynamic Constants of Some Metal Carbides

Carbide	Structure*	Lattice constants, Å			$\Delta H_{f25^\circ\text{C.}}^\circ$ kcal/mole	$\Delta F_{f25^\circ\text{C.}}^\circ$ kcal/mole	$\Delta S_{f25^\circ\text{C.}}^\circ$ cal/(mole)(°C)
		a_0	b_0	c_0			
Aluminum							
Al_4C_3	Rhombohedral	8.53			-30.9	-29.0	-6.4
Barium							
$\text{BaC}_2(\text{I})$	F.c.t.	6.22		7.06	-5.0	ca. -6.0	
BaC_2	F.c.c.	6.54					
Beryllium							
Be_3C	Cubic (antifluorite)	4.34					
Boron, B_6C	Rhombohedral	5.19					
	Hexagonal	5.60		12.12			
Calcium							
$\text{CaC}_2(\text{I})$	F.c.t.	5.48		6.37	-15.0	-16.2	4.0
(II)							
(III)							
(IV)	F.c.c.	5.92					
Cerium							
CeC_2	F.c.t.	3.87		6.48			
Chromium							
Cr_{23}C_6	F.c.c.	10.638			-98.4	-100.2	6.0
Cr_7C_3	Hexagonal	13.98		4.523	-42.5	-43.8	4.4
Cr_3C_2	Orthorhombic	2.821	5.52	11.46	-21.0	-21.2	0.7
Cobalt							
Co_3C	Orthorhombic	4.52	5.08	6.73	9.5	7.1	8.0
Co_2C					11.3		
Copper							
Cu_2C_2							
CuC_2							
Hafnium							
HfC	F.c.c.	4.4578					
Iron							
Fe_3C	Orthorhombic	4.5144	5.0767	6.7297	5.0	3.5	5.0
Fe_5C	Hexagonal	2.749		4.340			
Fe_3C Hägg	Orthorhombic	9.04	15.66	7.92			
Lanthanum							
LaC_2	F.c.t.	3.92		6.55			
Lithium							
Li_2C_2					-14.2		
Magnesium							
Mg_7C_3	Hexagonal	7.43		10.59	19.0		
MgC_2	F.c.t.	5.54		5.02	21.0	20.0	3.4
Manganese							
Mn_{23}C_6	F.c.c.	10.56					
Mn_7C_3	Hexagonal	13.87		4.53			
Mn_3C	Orthorhombic				-23.00	-23.12	0.4
Molybdenum							
Mo_7C	H.c.p.	2.994		4.722	4.3	2.9	4.7
MoC	Hexagonal	2.901		2.768			
Neodymium							
NdC_2	F.c.t.	3.82		6.23			
Nickel							
Ni_3C	Orthorhombic	2.646		4.329	9.2	8.9	1.0
Niobium							
NbC	F.c.c.	4.4584-4.462			-19.0		

Table 1.7.2 — (Continued)

Carbide	Structure*	Lattice constants, Å			$\Delta H_{f25^\circ\text{C}}^\circ$ kcal/mole	$\Delta F_{f25^\circ\text{C}}^\circ$ kcal/mole	$\Delta S_{f25^\circ\text{C}}^\circ$ cal/(mole)(°C)
		a_0	b_0	c_0			
Plutonium							
PuC	F.c.c.	4.920					
Pu ₂ C ₃	B.c.c.	8.129					
Praseodymium							
PrC ₂	F.c.t.	3.85		6.41			
Samarium							
SmC ₂	F.c.t.	3.75		6.28			
Scandium							
ScC	F.c.c.						
Silicon							
SiC (β)	F.c.c.	4.3590			-26.70	-26.12	-1.95
SiC (α)	(Wurtzite)	3.0817		5.0394			
4H, SiC(III)(α)	Hexagonal	3.079		10.254			
6H, SiC(III)(α)	Hexagonal	3.0817		15.1183			
15R, SiC(I)(α)	Hexagonal	3.079		37.78			
21R, SiC(IV)(α)	Hexagonal	3.079		52.88			
33R, SiC(VI)(α)	Hexagonal	3.079		83.10			
51R, SiC(V)(α)	Hexagonal	3.079		128.434			
87R, SiC (α)	Hexagonal	3.079		219.094			
Silver							
Ag ₂ C ₂	Amorphous				81.9		
Sodium							
Na ₂ C ₂					-9.66	-6.57	10.4
Strontium							
SrC ₂ (I)	F.c.t.	5.81		6.68			
SrC ₂ (II)							
SrC ₂	F.c.c.	6.24					
Tantalum							
Ta ₂ C	H.c.p.	3.091		4.92			
TaC	F.c.c.	4.445-4.56			-63.8		
Thorium							
ThC	F.c.c.	5.34					
ThC ₂	Monoclinic	6.53	4.24	6.56	-45.6	-50.2	15.4
Titanium							
TiC	F.c.c.	4.3189			-54.	-53.	-3.4
Tungsten							
W ₂ C (β)	H.c.p.	2.99		4.72	7.09	1.64	-18.3
WC	Hexagonal	2.90		2.83	-3.92	-3.4	-1.7
Uranium							
UC	F.c.c.	4.951			-40	-41	3.4
U ₂ C ₃	B.c.c.	8.088					
UC ₂	B.c.t.	3.517		5.987	-36	-38	6.7
Vanadium							
VC	F.c.c.	4.160			-28.0	-27.5	-1.6
Yttrium							
YC ₂	F.c.t.	3.79		6.58			
Zirconium							
ZrC	F.c.c.	4.673-4.688			-45.	-35.5	31.9

*F.c.t. = face-centered tetragonal; f.c.c. = face-centered cubic; h.c.p. = hexagonal close packed; b.c.c. = body-centered cubic; b.c.t. = body-centered tetragonal

Table 1.7.3—The Stability and Preparation of Some Metal Carbides

Carbide	Stability	Preparation
Aluminum		
Al_4C_3	Decomposes in water	$\text{Al} + \text{C}$; $\text{Al}_2\text{O}_3 + \text{C}$
Barium		
$\text{BaC}_2(\text{I})$	Stable below 150°C ; decomposes in water	$\text{BaCO}_3 + \text{C}$; $\text{BaO} + \text{C}$
BaC_2	Stable above 150°C	
Beryllium		
Be_2C	Attacked by moist air; decomposes in water; dil HAc; reacts with NH_3 , N_2 , O_2 , CO_2 above 1000°C	$\text{BeO} + \text{C}$ at 2100°C in He; $\text{Be} + \text{C}$ at 900°C – 1300°C in He or vacuum
Boron		
B_4C	Resistant to air to 1000°C ; oxidizes rapidly in oxidizing gases at high temperature	$\text{B}_2\text{O}_3 + \text{C}$; $\text{BN} + \text{C}$; $\text{B} + \text{C}$; $\text{BCl}_3 + \text{CO} + \text{H}_2$ over hot W or Mo wire; BCl_3 over hot C, with or without H_2
Calcium		
$\text{CaC}_2(\text{I})$	Stable at 25° – 450°C ; decomposes in water	Electrolysis of molten Ca salts; $\text{CaCO}_3 + \text{C}$; $\text{CaO} + \text{C}$; $\text{Ca} + \text{C}$
$\text{CaC}_2(\text{II})$	Stable below 25°C	
$\text{CaC}_2(\text{III})$		
$\text{CaC}_2(\text{IV})$	Stable above 450°C	
Cerium		
CeC_2	Decomposes in water	$\text{CeO}_2 + \text{C}$
Chromium		
Cr_{23}C_6		$\text{Cr} + \text{C}$
Cr_7C_3	Decomposes to Cr_{23}C_6 at 730° – 870°C	
Cr_3C_2		
Cobalt		
Co_3C	Metastable	$\text{Co} + \text{C}$; $\text{Co} + \text{CO}$ under 230°C ; $\text{Co} + \text{C}$ at 218°C
Co_2C	Unstable	
Copper		
Cu_2C	Unstable, decomposes spontaneously	Acetylene + Cu salt solution
CuC_2		
Hafnium		
HfC		HfH_2 in graphite crucible at 2100°C ; $\text{Hf} + \text{C}$; $\text{HfO}_2 + \text{C}$; Hf wire + C at 2000° – 2200°C ; HfCl_4 + toluol + W filament at 2100° – 2500°C
Iron		
Fe_3C	Metastable	$\text{Fe} + \text{C}$; $\text{CO} + \text{Fe}_2\text{O}_3$ at 550°C ; $\text{CO} + \text{Fe}_3\text{N}$ over 500°C
Fe_2C	Forms Hägg Fe_2C at 300°C	$\text{Fe} + \text{CO}$ at 170° – 240°C
Fe_7C Hägg	Forms Fe_3C at 550°C	$\text{CO} + \text{Fe}_3\text{N}$ below 500°C ; Fe catalysts + hydrocarbons at 275° – 325°C
Lanthanum		
LaC_2	Decomposes in water, H_2SO_4	
Lithium		
Li_2C_2	Ignites in SO_2 , CO_2 ; decomposes in water	$\text{Li}_2\text{CO}_3 + \text{C}$; $\text{Li} + \text{C}$
Magnesium		
Mg_2C_2	Reacts violently with water; decomposes at 800°C	$\text{Mg} + \text{pentane}$ at 700°C
MgC_2	Reacts with moist air; decomposes to Mg_2C_2 above 550°C	$\text{Mg} + \text{acetylene}$ at 450° – 500°C

Table 1.7.3 — (Continued)

Carbide	Stability	Preparation
Manganese		
$Mn_{12}C_6$	Metastable at 700°–750°C	Mn + methane; Mn + C
Mn_7C_3		
Mn_3C	Stable at 750°–950°C in 1 atm H_2 + CH_4 ; decomposes in H_2O	
Molybdenum		
Mo_2C		Mo + C at 1200°C; Mo + methane at 700°–850°C; $MoO + CaC_2$
MoC	Decomposes to Mo_2C at 950°C	Mo + C at 1500°–1600°C in H_2 or N_2
Neodymium		
NdC_2	Decomposes in water	$Nd_2O_3 + C$
Nickel		
Ni_3C	Decomposes in water; stable below 300°C; stable in N_2 to 380°–420°C	Ni or Ni oxides + CO or hydro- carbons at 170°–250°C
Niobium		
NbC	Stable to 2500°C in N_2 ; decomposes in HF	NbH in graphite crucible at 2100°C; Nb + C
Plutonium		
PuC		
Pu_2C_3		
Praseodymium		
PrC_2	Decomposes in water	$Pr_2O_3 + C$
Samarium		
SmC_2	Decomposes in water	$Sm_2O_3 + C$
Scandium		
ScC		
Silicon		
$SiC (\beta)$	Forms below 2500°C; oxidizes slowly in air	Si + C above 1200°C; $SiO_2 + C$ at 1475°C; $SiCl_4$ + toluene + H_2 + hot C filament
$SiC (\alpha)$		
4H, $SiC(III)(\alpha)$	Stable above 2000°C; oxidizes slowly in air; attacked by oxides and molten metals at high temperature	β -SiC at 2100°C; Si + C at 2500°– 2300°C; coke + sand + SiO_2 at 1800°–2000°C
6H, $SiC(III)(\alpha)$		
15R, $SiC(I)(\alpha)$		
21R, $SiC(IV)(\alpha)$		
33R, $SiC(VI)(\alpha)$		
51R, $SiC(V)(\alpha)$		
57R, $SiC (\alpha)$		
Silver		
Ag_2C_2	Light sensitive; decomposes in dil HCl; ex- plosive when heated	Acetylene + Ag salt solution
Sodium		
Na_2C_2	Ignites in SO_2 , CO_2 ; decomposes in water, alcohol	Acetylene + Na in vacuum or in H_2 at 220°C
Strontium		
$SrC_2(I)$	Decomposes in water, acid; stable at –30° to 370°C	$SrCO_3 + C$; $SrO + C$
$SrC_2(II)$	Stable below –30°C	
SrC_2	Stable above 370°C	
Tantalum		
Ta_2C		Ta + C at 1600°C in H_2 ; $Ta_2O_5 + C$ at 1700°C in H_2 or at 1600°C in vacuum

Table 1.7.3—(Continued)

Carbide	Stability	Preparation
TaC	Decomposes in HF; attacked by aqua regia and O ₂ at high temperatures	Ta + C at 2200°C; TaCl ₄ + toluol + W filament at 900°–1000°C; Ta wire at 2300°–2900°C in CH ₄ or C ₂ H ₂ ; TaH in graphite crucible at 2100°C
Thorium ThC ThC ₂	Decomposes in water, dil acid; burns in air, sulfur	Th in graphite crucible at 2400°–2450°C or at 2100°C in vacuum; ThO ₂ + C
Titanium TiC	Oxidizes readily with oxidizing gases at high temp.; stable to 2500°C in N ₂	Ti + C; TiO ₂ + C at 2100°C in H ₂ ; TiO ₂ + C at 1650°C in vacuum; TiCl ₄ + toluol + W filament at 1630°–2000°C; TiH ₂ in graphite crucible at 2150°C
Tungsten W ₂ C (β) WC		WO ₃ + C or CaC ₂ W + C at 1400°–1500°C in H ₂ ; WO ₃ + C or CaC ₂ ; W + C gases at 860°C
Uranium UC	Stable at room temperature	U + UC ₂ above 1900°C; U + methane at 625°–900°C; U + C at 2100°C; U ₂ O ₃ + C at 1800°C
U ₂ C ₃	Stable at –196° to 1800°C	UC + UC ₂ at 1250°–1800°C with stressing
UC ₂	Decomposes in water, acid, alkali; ignites in air, O ₂ , N ₂ , Cl ₂ , Br ₂	UO ₂ + C above 2400°C; U + C at 2400°C; U ₂ O ₃ + C at 2400°C
Vanadium VC	Burns in O ₂ ; stable to 2500°C in N ₂	V ₂ O ₅ + C or CO below 1800°C; VCl ₄ + toluol + W filament at 1500°–2000°C
Yttrium YC ₂	Decomposes in water	Y ₂ O ₃ + C
Zirconium ZrC		ZrO ₂ + C at 1900°–2200°C; Zr + C; ZrCl ₄ + toluol + W filament at 1700°–2400°C; ZrH ₂ in graphite crucible at 1700°–2100°C

Table 1.7.4—Selected Properties of the Common Carbides

Carbide	Electrical resistance at room temp., ohm-cm	Thermal conductivity at 100° to 800°F (Btu/hr/sq ft)/(°F/in.)	Coefficient of linear thermal expansion at 78° to 1100°F, per °F	Modulus of rupture at room temp., lb/sq in.	Tensile strength, lb/sq in.		Thermal shock resistance cycles before failure				Satisfactory methods of fabrication	
					1800°F	2200°F	1800°F	2000°F	2300°F	2400°F		
Beryllium Be ₂ C	6.3 × 10 ⁻²	9.2	10.5 × 10 ⁻⁶	16,000	4 cycles at 2000-1475°F				*†,‡	
Boron B ₄ C	...	650	2.6 × 10 ⁻⁶	...	22,500	...	½**	*§
Chromium Cr ₃ C ₂	50,000	*
Hafnium HfC	1.09 × 10 ⁻⁴
Molybdenum MoC	*
Silicon SiC	1.07 × 10 ²	250	4.3 × 10 ⁻⁶	100 cycles at 2500-75°F				*†,§,¶	
Tantalum Ta ₄ C	*
TaC	2 × 10 ⁻⁶
Titanium TiC	...	240	4.1 × 10 ⁻⁶	...	17,200	9,400	25**	25	25	21	...	*†
Uranium UC ₂	...	238
Vanadium VC	1.56 × 10 ⁻⁶
Tungsten W ₂ C	8.1 × 10 ⁻⁶
WC	1.2 × 10 ⁻⁶	*†
Zirconium ZrC	6.34 × 10 ⁻⁶	...	3.7 × 10 ⁻⁶	...	14,450	15,850	22**	*†

*Hot pressing

†Steel die pressing and sintering

‡Hydrostatic pressing and sintering

§Extrusion and sintering

¶Slip casting

**1 cycle = 10 min at testing temp. followed by air quench at 89°F for 5 min

SELECTED READING LIST

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CHAPTER 1.8

Cements and Concretes

M. J. Snyder

In the ordinary sense of the word, concrete consists of a cementing phase and an inert filler called the "aggregate." Portland cement is the most widely used cementing phase, although many other cements have been studied for use in shields. Sand and gravel are used as aggregates in ordinary concrete construction. For shielding work, heavier aggregates are commonly used to produce a heavier concrete.

REACTOR APPLICATION

Cement and concrete have been employed extensively for shielding large stationary reactors, such as those at Oak Ridge and Brookhaven, for shielding equipment in radiochemical laboratories and plants, and for shielding cyclotrons. Cement and concrete have been used both in the monolithic form and in the block form. The standard concrete block used in the building trade and special large blocks have been employed at various installations.

COST AND AVAILABILITY

The cost of a concrete shield is dependent on several factors: (1) the cost of the materials from which the concrete is fabricated, (2) the amount of concrete required to do the shielding, (3) the method of fabricating the shield, and (4) tolerances in the dimensions and positioning of the apertures in the shield. Data on the cost of the materials for several concretes, which have been used or proposed for shielding, are given in Table 1.8.1.

The material costs for high-density concretes are appreciably higher than the cost for ordinary concrete. In many cases, however, the cost might be reduced by using less costly forms of the heavy aggregate, for example, by using an ungraded iron shot or punchings containing irregularly shaped pieces. The effect of such substitutions on the quality of the concrete needs to be determined. The use of cementing phases other than Portland cement (magnesium oxychloride, for example) generally also leads to increased material costs. The shielding advantages to be derived from substituting for Portland cement a cement of higher water content (increasing the hydrogen content), greater density, or different cross section are debatable. Some of the later shielding measurements indicate that large differences in the water content of a concrete have only a slight effect on the shielding properties.

As a rough approximation, the ratio of the densities of two shielding materials can be used as a criterion of their gamma-shielding power (this is true only at 1 to 3 mev and may be incorrect by a factor of 3 or more at other energies). This approximation may be used to obtain a crude idea of the comparative cost of shields made of different concretes.

Table 1.8.1 —Cost of Materials in Concretes for Shielding

(T. Rockwell III and A. S. Kitzes, Theoretical and Practical Aspects of Shielding, ORNL-710, Sept. 29, 1950)

Material*	Cost, cts/lb	Density, [†] gm/cm ³
Ordinary concrete block	0.31	2.22
Brookhaven concrete	3.0	4.3
Portland cement with fine magnetite aggregate	1.0	3.0
Portland cement with iron-sand aggregate	2.5	4.7
Portland-barytes concrete	1.0	3.5
Magnesium oxychloride-iron shot concrete	3.0	5.8

*See Tables 1.8.4 and 1.8.5 for composition

[†]Gm/cm³ × 62.43 = lb/cu ft

A more realistic cost appraisal will depend upon the amount of concrete required and the best method of constructing the shield, which, in turn, depend upon the measured shielding properties in terms of the specific source to be shielded, the space and weight requirements, and the complexity of the shield. Where monolithic construction is employed, the cost of erecting forms and positioning through-tubes and the like may be important. If the shield is built from blocks, the cost of fabricating the blocks and laying the mortar joints must be added to the cost of materials.

Portland cement and the materials that go into magnesium oxychloride cement are readily available. Many of the special cements that have been studied for shielding applications are laboratory curiosities, and development work would be needed to make them commercially available. Generally, the heavy aggregates that have been used are readily available.

SHIELDING PROPERTIES

For a detailed presentation of reactor-shielding theory, the reader is referred to Vol. 1, Sec. 2, of this Handbook. Discussions of shielding problems have been collected in other works.¹

Calculating the shielding efficiency of a concrete shield is an arduous task at best, and a complete analytical design of a shielding installation is not possible at present. The design of shielding for specific reactors is guided by data obtained on the attenuation of neutrons and gamma radiation by large slabs of materials. Data on the neutron attenuation characteristics of several concretes that have been used or proposed for shielding are given in Table 1.8.2.

The composition of concrete can be changed rather readily to meet the dictates of nuclear requirements. Boron can be added (in M-1 concrete, for example) as an inert aggregate in the form of colemanite. Other materials of high cross section might be added similarly as aggregate or as components of the cementing phase. The distribution of the elements in and the compositions of various cements are shown in Tables 1.8.3 and 1.8.4, respectively. The hydrogen content of the shield can be increased by replacing Portland cement with magnesium oxychloride cement, which has a higher water content. Data on the hydrogen content, determined as water, of typical cements as a function of tempera-

¹Reference appears at end of chapter.

ture are given in Fig. 1.8.1. Most of the cements that have been proposed for shielding use have appreciably higher hydrogen contents than Portland cement. Although increasing the water content above that of Portland cement does not seem to improve neutron attenuation, the use of a cement with higher water content permits higher density concretes to be built with the same net water content. A denser cement phase (for example, barium cement or litharge-glycerin cement) can be used; however, the density of the concrete is increased only slightly by increasing the cement density, since the cement phase constitutes only about 15 percent of the total in high-density concretes.

Table 1.8.2— Neutron-attenuation Characteristics of Shielding Materials*

[R. Zirkind, Technical Summary of All ORNL Summer Shielding Sessions (1949),
ORNL-503, June 19, 1950]

Shield material	Density, gm/cm ³	Attenuation range †	Relaxation length, ‡ cm
Magnesium oxychloride concrete	5.6	10 ⁷	6.0
M-1 concrete§	4.5	10 ⁶	5.8
Brookhaven concrete	4.3	10 ⁵	6.3
Boron cement¶	2.0	10 ⁶	7.6

*The radiation emanating from a core hole in the shield of the X-10 reactor was used as a neutron source; gold-foil activity was used to measure neutron attenuation

†Attenuation range is reduction of intensity of neutron flux by thickness of specimen used

‡Relaxation length is the length in which the neutron intensity is reduced by a factor of e

§Magnesium oxychloride concrete containing 1 percent of boron as colemanite

¶Cement phase of M-1 concrete

MECHANICAL PROPERTIES

The service conditions that a shield must withstand vary with the application. For large stationary reactors in permanent buildings, the only mechanical requirement is that the shield support its own weight, withstand any unusual stresses imposed by its geographic location, and not undergo deterioration with time which would permit harmful amounts of radiation to escape. Resistance to heat, thermal shock, strength, and the like are of slight importance. In other applications, such as in mobile reactors or in shields for isotope shipments, these factors may be important. The available data on the mechanical properties of cements and concretes for shielding are presented in Tables 1.8.5 to 1.8.10. Many of the cements and concretes have not been examined thoroughly because of their high cost or lack of promise for large-scale use. The comparison of values for mechanical properties of cements and concretes is complicated by the fact that the method of fabrication of the specimen (degree of consolidation, amount of tempering water, and the like) and the curing conditions affect the result. Also, there are no standard test methods for many of the properties measured. Each laboratory has developed its own method for measuring several of the properties, and these properties may be reported in different units for different cements.

Generally, the mechanical properties of heavy concretes prepared with Portland cement are not appreciably different from those of ordinary Portland concrete, and both types of concrete can be expected to withstand about the same service conditions. Heavy concretes prepared from magnesium oxychloride have higher strengths than Portland base concretes,

Table 1.8.3—Elements Contained in Appreciable Quantities in Various Cements*

Element	Cement No.†									
	1	2	3	4	5	6	7	8	9	10
Al	x			x	x		x		x	x
B			x							
Ba							x			
Br				x						
C								x		
Ca	x		x						x	x
Cd				x	x					
Cl		x	x	x	x					
Co				x						
Cr				x						
Cu						x				
Fe									x	
Hg						x				
Mg		x	x	x						
Mn					x	x				
Ni				x						
P						x				
Pb						x		x		
S				x	x					
Si	x						x		x	x
Sn						x				
V						x				
Zn					x	x				

*All contain hydrogen and oxygen

†See Table 1.8.4 for composition of cements

Table 1.8.4—Composition of Cements

Cement No.	Name	Composition
1	Portland	Hydrated calcium aluminosilicate
2	MO*	Magnesium oxide tempered with magnesium chloride solution
3	Boron	Magnesium oxide and colemanite tempered with magnesium chloride solution
4	Magnesia	Magnesium oxide tempered with solutions of one or more of the following salts: $\text{Al}_2(\text{SO}_4)_3$, CdSO_4 , CoCl_2 , CoSO_4 , $\text{Cr}_2(\text{SO}_4)_3$, CrCl_3 , MgBr_2 , NiCl_2 , NiSO_4
5	Oxyacid	The following oxides tempered with solutions of their chloride or sulfate salts: Al_2O_3 , CdO , MnO , ZnO
6	Phosphate	The following oxides tempered with a solution of phosphoric acid: CuO , Cu_2O , HgO , MnO , PbO , Pb_2O_4 , SnO , V_2O_5 , ZnO
7	Barium	Hydrated barium aluminosilicate
8	Litharge glycerin	Litharge (PbO) tempered with glycerol
9	Iron cement	High-iron Portland cement
10	Lumnite	High-alumina Portland cement

*Magnesium oxychloride

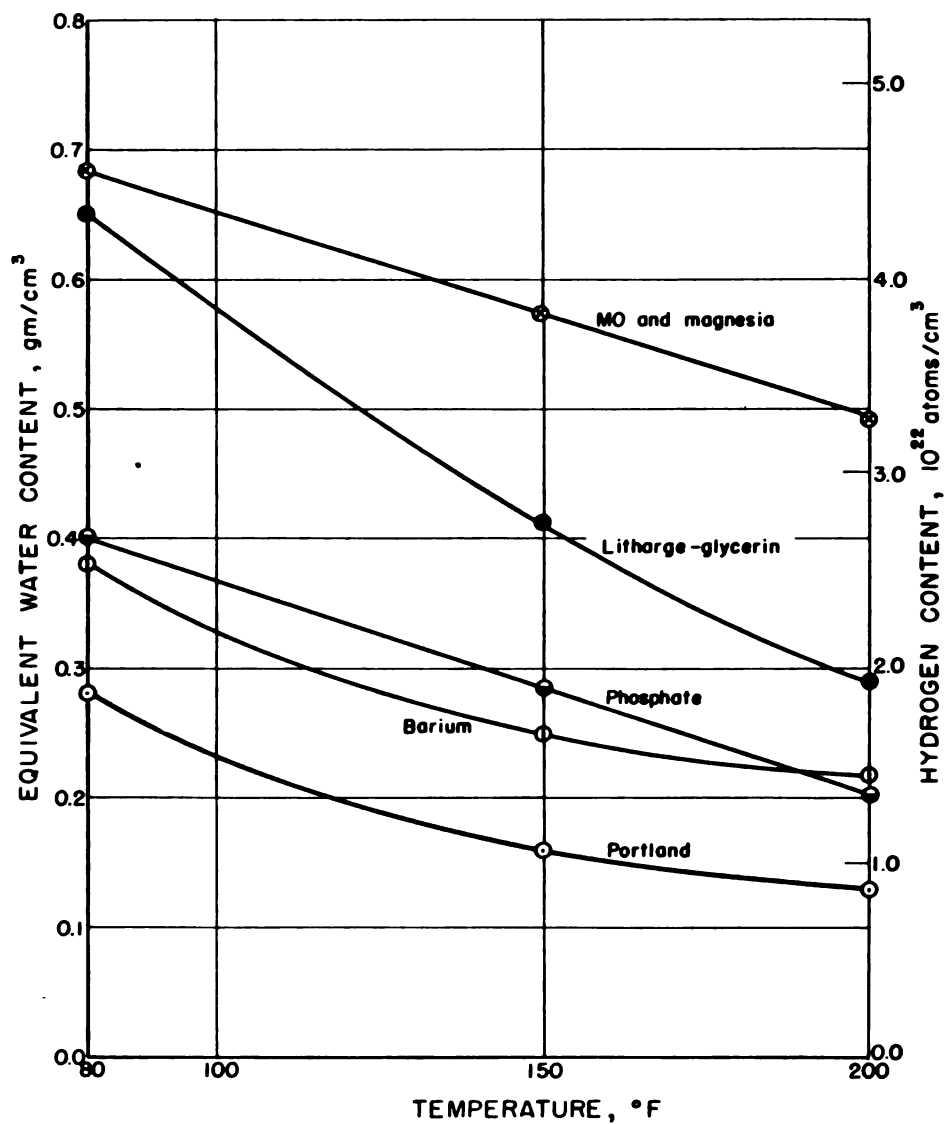


Fig. 1.8.1 — Hydrogen Content of Various Cements. Submitted by Battelle Memorial Institute, June 10, 1952. (MO—Magnesium Oxychloride.)

Table 1.8.5—Composition of Concretes

Name	Material composition				Elemental composition,* mg-atom/cm ³												
	Cement Phase		Aggregate		Water, %	Fe	H	B	O	Mg	Cl	Ca	Si	Al	Mn	S	C
	Type	%	Type	%													
Plain Portland	Portland	15.0	Sand	34.2	7.5	0.13	4.76 (±20%)	...	71.8	0.2	...	14.5	15.6	0.44	...	0.06	10.8
Brookhaven†	Gravel		Gravel	43.3													
	Portland	13.0	Limonite	26.0	4.0	54.7	21.1 (±20%)	...	47.7	0.35	...	6.45	2.10	0.79	1.22	0.11	...
MO‡	Steel		Steel														
	punchings		punchings	57.0													
M-1**	Steel shot	7.0§	Steel shot	40.0	7.6¶	88.3	26.3 (±15%)	...	21.1	8.69	2.05	0.37
	Steel		Steel														
Portland iron‡	punchings		punchings	53.0													
	Colemanite	6.5§	Colemanite	6.5	6.0††	68.5	35.9 (±5%)	3.91	32.0	8.5	2.89	1.29	0.28
Portland iron‡	Steel		Steel														
	punchings		punchings	77.0													
Boron cement	Steel shot	11.6	Steel shot	36.5	3.5												
	Steel		Steel														
Boron cement	punchings		punchings	48.4													
	Colemanite	50.0§	Colemanite	50.0	4.5††	...	79.1 (±5%)	7.98	68.2	16.42	...	6.93	2.66

Not available

*R. Zirkind, Technical Summary of All ORNL Summer Shielding Sessions (1949), ORNL-503, June 19, 1950

†C. R. Binner, C. B. Wilkie, and P. Miller, High-Density Concrete Shielding, HKF-1, Feb. 15, 1949

‡M. J. Snyder, C. A. Burkart, and J. W. Clegg, Engineering Properties of High-Density Concretes, BMI-71, May 1951. (MO-magnesium oxychloride.)

§As magnesium oxide. Percentage of dry batch

¶As 26° Bé MgCl₂ solution. Percentage of dry batch

**E. C. Miller, editor, Technical Division: Report for Quarter Ending February 28, 1949, ORNL-323, Feb. 28, 1949

††As saturated MgCl₂ solution. Percentage of dry batch

Table 1.8.6—Mechanical Properties of Concretes*

Property	MO†	Brookhaven	Portland, iron aggregate	Ordinary Portland
Density,‡ gm/cm³	5.3–5.6	4.3–4.5	5.5	2.4
7-day compressive strength, lb/sq in.	5000–10,000	4800	2900	2500
Modulus of elasticity,§ 10⁶ lb/sq in.	5.4	3.5	4.4	4.0
Flexural strength, lb/sq in.	1200–1500	490–640	616	400
Shear strength, lb/sq in.	...	833	...	590
Bonding strength,¶ lb/sq in.	250	650	...	575

*See Table 1.8.5 for composition of concretes

†Magnesium oxychloride

‡Gm/cm³ × 62.43 = lb/cu ft

§Secant modulus at a stress of 2000 lb/sq in., compression

¶Maximum stress in pull-out test using a plain steel rod

Table 1.8.7—Strength and Density of Miscellaneous Cements

(M. J. Snyder, C. A. Burkart, and J. W. Clegg, Investigation of Cementitious Materials for Possible Use in Concretes for Pile Shielding, BMI-T-21, September 1949)

Cement	7-day Compressive strength, lb/sq in.	Density,* gm/cm³
MgO + MgCl₂	9290	1.92
MgO + CrCl₃	1870	...
MgO + Al₂(SO₄)₃	1470	2.02
MgO + Cr₂(SO₄)₃	3190	2.22
MgO + CoSO₄	2320	2.17
MgO + NiSO₄ + NiCl₂	2950	...
Barium Portland	6520	3.07
Litharge glycerin	4500	4.31

*Gm/cm³ × 62.43 = lb/cu ft

Table 1.8.8—Thermal Properties of Concretes and Cements*

Property	Concrete			Cement	
	MO†	M-1	Brookhaven	MO†	Portland
Specific heat,‡ Btu/(lb)(°F)	0.144	0.164	0.166	...	0.156
Thermal conductivity,§ Btu/(hr)(ft)(°F)	2.9	1.8	1.6–2.1	...	1.2
Thermal expansion, per °F	10 × 10⁻⁶	11 × 10⁻⁶	6.8 × 10⁻⁶	12 × 10⁻⁶	6.6 × 10⁻⁶

*See Table 1.8.5 for compositions

†Magnesium oxychloride.

‡Btu/(lb)(°F) × 1 = cal/(gm)(°C)

§Btu/(hr)(ft)(°F) × (4.13 × 10⁻³) = cal/(sec)(cm)(°C)

Table 1.8.9—Dimensional Stability of Concretes

Type	Stability
Ordinary Portland	Extremely stable, dimensional change less than 0.05 percent on 1 yr storage, resistant to weathering
MO*	Stability varies with type of magnesia and concentration of magnesium chloride used; dimensional change of about 0.1 percent on 1 yr storage; not suitable for exterior exposure†
M-1	Stability about same as for MO
Brookhaven	Stability similar to that of ordinary Portland; punchings may rust where exposed

* Magnesium oxychloride

† M. J. Snyder, C. A. Burkart, and J. W. Clegg, Dimensional Stability of Magnesium Oxychloride Cements and Concretes, BMI-T-45, 49 pp, Secret, July 1950

Table 1.8.10—Heat Resistance of Concretes

Type of concrete or cement	Heat resistance
Ordinary Portland concrete	Will withstand up to 500°F structurally
Brookhaven concrete	Will withstand temperature differential of 350°F between center and outside of 6-in.-diameter cylinder
MO* concrete	Strength decreases with temperature but will withstand 600°F
Lumnite cement	Better mechanical properties than Portland cement above 800°F

* Magnesium oxychloride

but considerable doubt exists as to their stability. No long-time service tests have been made of concretes prepared with MO* cement, and the results of short-time tests have been highly variable. Further development work on these concretes may lead to satisfactory stability and enable their use in the more critical shielding applications. Several of the laboratory cements offer promise on the basis of the limited information available, but much development work is needed before they can be considered for large-scale use.

Only a very limited amount of work has been done on radiation damage to concrete shielding. Portland concrete (around the X-10 reactor, for example) is not damaged by radiation. Data on MO* concrete are indefinite (in some cases, no effect; in other cases, gas evolution) and no data are available on other concretes.

FABRICATION OF CONCRETE SHIELDS

Ordinary concrete practices, with a few modifications needed because of the high density, have been used in casting shields or shielding blocks. The standard texts should be consulted for information on the usual procedures. The volume of cement that can be handled in mixing equipment is decreased because of the higher density, and the amounts of materials remaining in the mixer thus become a matter of concern. These problems can be eliminated by using different techniques in mixing and placing the concrete. The heavy

* Magnesium oxychloride.

aggregate can be placed in the form and the cement poured over it and consolidated by rodding and vibration, or the cement can be poured into the form and then the aggregate added with rodding and vibration. Where cements other than Portland are employed, setting time may be of importance. Difficulty in casting large slabs of magnesium oxychloride has been experienced as a result of premature setting of the cement. The setting times of many of the cements that are at a laboratory stage of development are considerably less than that of Portland, and difficulty with premature setting might be expected unless effective retarders are developed.

Where very large sections are cast, the heat liberated on setting may cause cracking. This problem has been solved in constructing large concrete dams either by cooling through imbedded pipes or by careful control of the pouring schedule to permit escape of the liberated heat. Data on the handling characteristics of various concretes are given in Table 1.8.11.

Table 1.8.11 — Handling Characteristics of Various Concretes

Characteristic	Concrete			
	Portland	Brookhaven	MO*	M-1
Initial set, hr	12	8	8	10
Days to attain 80% of final strength	7	7	1	1
Heat of setting, Btu/lb	~3	~3	7.6†	~5†
Adiabatic temperature rise during setting, °F	...	43
Shrinkage on setting, %	0.2	0.2	‡	‡
Best workability slump, in.	4	3	7	8

* Magnesium oxychloride

† The heat liberated on setting is a function of the grade of magnesia and the concentration of the magnesium chloride. Heat liberation 12 times as great as the tabular value has been reported. A stable composition liberates about the same amount of heat as Portland cement

‡ Shrinkage on setting varies with grade of magnesia and concentration of magnesium chloride solution. Compositions that produce stable concretes shrink or expand less than 0.1 percent on setting

REFERENCE

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CHAPTER 1.9

Graphite

J. A. Slyh

REACTOR APPLICATION

Elemental carbon may be employed with considerable success in heterogeneous nuclear reactors as a moderator and as a reflector because of its low atomic weight, low neutron-absorption cross section, and high neutron-scattering cross section. Manufactured carbon products are predominantly of two types, both of which may be made of the same raw materials. When the material is heated only to 2750°F, it is known as "industrial carbon." It is extremely hard and has a low thermal conductivity and high electrical resistivity. When the material is heated to 4500°F or higher, it is known as "artificial graphite," "electro-graphite," or simply "graphite"; this product is easily machined and has a high thermal conductivity and a low electrical resistivity. Large quantities of both types of carbon are used commercially. However, owing to the ease of machining and the somewhat greater purity of artificial graphite, the data in this chapter pertain primarily to this form.

The high strength of graphite at elevated temperatures, its exceedingly high melting point, and its excellent resistance to rupture by thermally induced stresses make the material of potentially great value in high-temperature reactors and possibly in auxiliary associated equipment. In homogeneous reactors, graphite is proposed to serve as the continuous phase of solid fuel elements and to contribute a moderating value in addition to a structural value. Graphite is susceptible to radiation damage at low temperatures and to corrosion by certain fluids at high temperatures. This should be recognized by the design engineer.

ABUNDANCE AND AVAILABILITY

Carbon is estimated to rank twelfth or thirteenth among the elements in abundance. It occurs naturally in the free state as diamond and natural graphite and is found in combination with other elements as petroleum, coal, lignite, natural gas, carbon dioxide, vegetable matter, and animal matter.

Natural graphite frequently is converted to useful commercial articles by mixing the comminuted material with a bonding agent, forming to the desired shape, and heating to obtain permanency. Most deposits of natural graphite, however, are very impure, usually containing more than 10 percent of contaminants; therefore, such manufactured products are useful chiefly in applications which do not require high purity. Processes for purifying natural graphite are available and are employed commercially, but in consideration of the vast quantities of nearly pure carbon in the form of petroleum and coal derivatives, only specialized graphite products, which require the peculiar characteristics of natural

graphite, warrant this expensive processing. Very high density graphites having bulk densities greater than 2.0 gm/cm^3 have been prepared recently from purified natural graphite. These products, however, are highly anisotropic and have very low strengths. Consequently, a large industry has been developed to manufacture carbon and graphite products from petroleum coke, a by-product of petroleum refineries. When these products are heated to very high temperatures (4500° to 5500°F), the resulting material is artificial graphite. Because this high-temperature treatment is an electric-furnace operation, the factories are located in areas having an abundance of low-cost power. The artificial-graphite production capacity in the United States is over 100,000 tons/yr.

PREPARATION

COMMERCIAL PREPARATION

Items fabricated from carbon and artificial graphite are made of a filler and a binder which is shaped and heat treated to impart permanency. Prominent among the raw materials employed as fillers are petroleum coke, coal, and gas or petroleum blacks. Binders may be any hydrocarbonaceous material which distills destructively and leaves a carbon residue. Phenol formaldehydes, furfurals, starches, sugars, lignocelluloses, and petroleum and coal asphalts or tars are typical examples. Owing to economic considerations, however, petroleum and coal derivatives are used almost exclusively.

The filler and binder are mixed intimately at a temperature suitable for fluidization of the binder; the resultant mass is formed to shape by molding or extrusion; and the shapes then are baked at 1450° to 2750°F to set the binder carbon. At this stage, the product is known as carbon and is used in some applications in this form. Subsequent processing, depending on the ultimate use, may include impregnation with coal-tar pitch or metal and/or reheating. Impregnation with pitch is employed to increase the bulk density of the product. Impregnation with metal is employed for special applications such as electrical contacts and bearings. Reheating temperatures depend on the type of impregnant. When no metals are involved, the reheat temperature frequently is in the range of 4200° to 5500°F , and the resultant product if made of petroleum coke bonded with coal tar is artificial graphite. If the filler material is gas- or petroleum-black, the product, regardless of binder or temperature of heat treatment, has few or none of the typical properties of graphite, such as greasy feel and high thermal and electrical conductivity. Other raw materials give products which vary between these extremes in receptivity to graphitization.

The purity of the product depends upon the purity (inorganic content) of the raw materials and the temperature of heat treatment. Commercial carbon products (those heated to 2725°F or lower) vary in ash content, on ignition, from 0.5 to 9 percent. Artificial graphites vary from 0.04 to 0.5 percent. The residual contaminating metal usually is present as the carbide or hydroxide depending on the stability of the carbide in moist air.

PREPARATION FOR REACTOR USE

Owing to the high neutron-absorption cross section of the usual contaminants in graphite, a product containing as little foreign matter as possible is required for most applications in reactor design. All graphite in the reactors constructed to date has been made by the process described above for artificial graphite. Acceptable purity has been obtained by careful selection of the type of petroleum coke and coal tar and by particular control of the atmosphere in the graphitizing furnace. Reactor grades AGHT and AGOT are controlled in this manner (see Table 1.9.1).

GRADES OF GRAPHITE

Published values of the properties of graphite often are confusing because of the existence of a wide variety of grades. Each manufacturer has a series of number and letter designations for his products. The extruded grades vary in fineness of grain with the diameter of the electrode; the larger the diameter, the coarser the grain. In practically all

Table 1.9.1 — Ash and Impurity Contents of Artificial Graphite

Grade	Ash	Chemical analysis, ppm					
		B	Al	Ca	Ti	Fe	V
AGX*	1500	1.3	20	2000	50	40	70
C-18*	1200-2000	1.0	10	1200	35	100	200
AGHT†	700-1700	500	100	<100	<100
AGOT†	350-700	100-200	<100	<100	<100
CS†	350-700	<100

*Typical commercial graphite

†Normal reactor graphite

cases, molded blocks are fine-grained, usually finer than the finest of the electrodes. For a given fineness, density may vary considerably depending on impregnation treatment.

Special grades for nuclear application are AGOT and AGHT. These are processed like commercial electrodes of comparable diameter except that raw materials are more carefully selected and petroleum coke is used instead of metallurgical coke as a blanket during graphitization. The AGOT material is taken from the center of the furnace and the AGHT from the ends and edges. Some subdesignations of AGOT are made on the basis of the different cokes and pitches used; i.e., AGOT-W is prepared from Whiting refinery coke and Barrett No. 30 pitch.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants of various graphites are given in Table 1.9.2.

CRYSTALLOGRAPHY

The generally accepted structure of graphite is hexagonal with the atoms 1.42Å apart. The atoms are in parallel plane layers spaced 3.36Å apart. The layers are displaced in their planes so that the center of each hexagon has, directly above and directly below it, a carbon atom of an adjacent layer. In this configuration, one hexagon is directly above another hexagon in every third plane. There is some indication from x-ray diffraction data that a small fraction (3 to 12 percent depending on the sample) of the graphite in any given sample has a crystal structure differing only from the structure just described in that the hexagons in successive layers are displaced equally so that every fourth layer

Table 1.9.2 — Physical and Chemical Constants of Graphite

Thermal neutron-absorption cross section, millibarns/atom		
AGOT		4.8
Density,* † gm/cm ³		
Calculated from lattice constants		
Artificial		2.27–2.28
Natural		2.27–2.28
Helium displacement		
Artificial		2.10–2.17
Natural		2.26
Commercial electrodes‡		1.55–1.90
Commercial blocks‡		1.55–1.75
AGHT‡		1.61–1.65
AGOT‡		1.65–1.72
Melting point		Sublimes
Boiling point		Sublimes
Sublimation temperature, °C		3650 ± 25
Vapor pressure		§
Heat of vaporization, kcal/mole		143
Heat of sublimation, kcal/mole		140–170
Specific heat (C _p)¶, cal/(mole)(°C)		
25°C		2.066
127°C		2.851
327°C		4.03
527°C		4.75
727°C		5.14
927°C		5.42
1127°C		5.67
Enthalpy (H°–H° _{–273.16°C}), cal/(mole)		
25°C		251.56
127°C		502.6
327°C		1198.1
527°C		2081.7
727°C		3074.6
927°C		4130
1127°C		5242
Entropy (S°–S° _{–273.16°C}), cal/(mole)(°C)		
25°C		1.3609
127°C		2.081
327°C		3.474
527°C		4.740
727°C		5.846
927°C		6.807
1127°C		7.663
	<u>Parallel</u>	<u>Perpendicular</u>
Electrical resistivity, μohm-cm		
Commercial electrodes**	850–1250	
Commercial blocks**	850–1100	
AGHT	800	1050–1250
AGOT	500–850	
CS	800	
GBF	720	

Magnetic susceptibility

Graphite is diamagnetic. The magnetic susceptibility values vary markedly between the "a" and "c" axes of the crystals; thus, owing to the variable anisotropy of graphite, duplication of measured values on different samples is difficult. To make magnetic susceptibility measurements useful, the invariant property of "total" susceptibility, X_T , has been determined. X_T is the sum of the susceptibilities determined in the three orthogonal

Table 1.9.2 — Continued

but otherwise arbitrary directions of the magnetic field with respect to the sample, and has a value of -21.0×10^{-6} for artificial graphites and manufactured carbons

Coefficient of thermal expansion, per °C

††

Thermal conductivity, cal/(sec)(cm)(°C)‡‡

§§

*Gm/cm³ × 62.43 = lb/cu ft

†See Fig. 1.9.1 for temperature-density relationship

‡Densities greater than 1.55 are obtained by impregnating with pitch

§See Fig. 1.9.2

¶Cal/(mole)(°C) × 1.0 = Btu/(lb-mole)(°F)

**Commercial "carbon" electrodes and blocks (heated not higher than 1500°C) have electrical resistivities 4 to 5 times as great as the artificial graphites quoted here

††See Fig. 1.9.3

‡‡Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(ft)(hr)(°F)

§§See Figs. 1.9.4 and 1.9.5

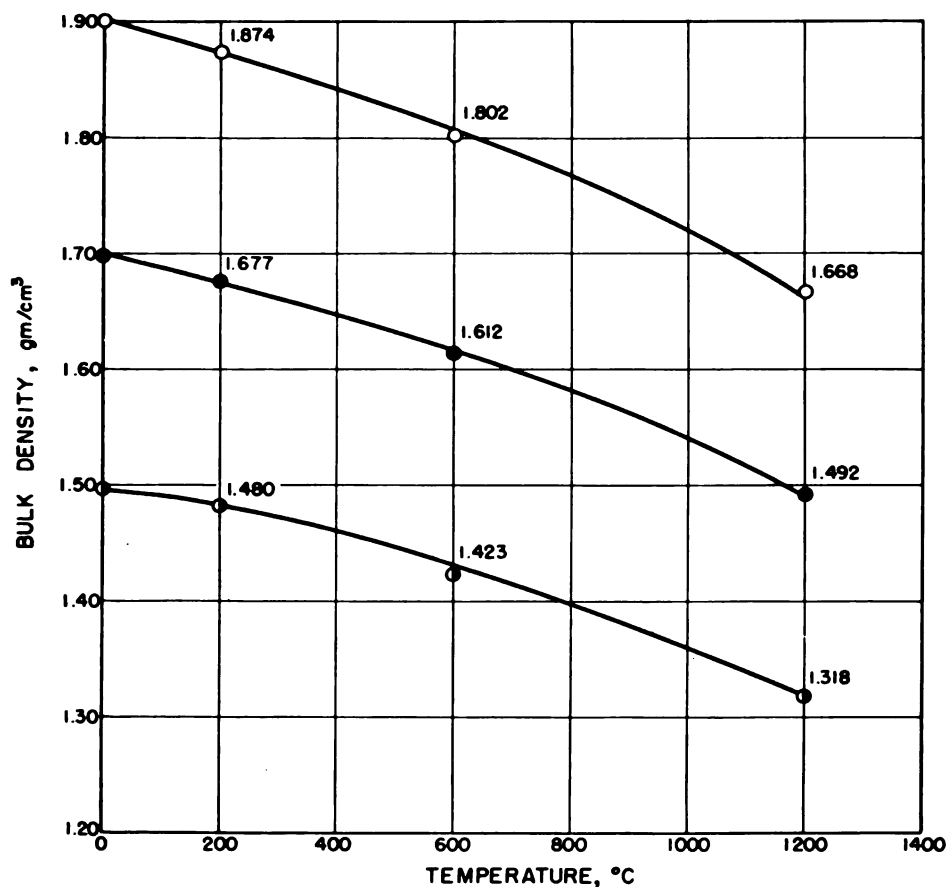


Fig. 1.9.1 — Variation of Graphite Bulk Density With Temperature. Submitted by Battelle Memorial Institute, Sept. 1, 1952.

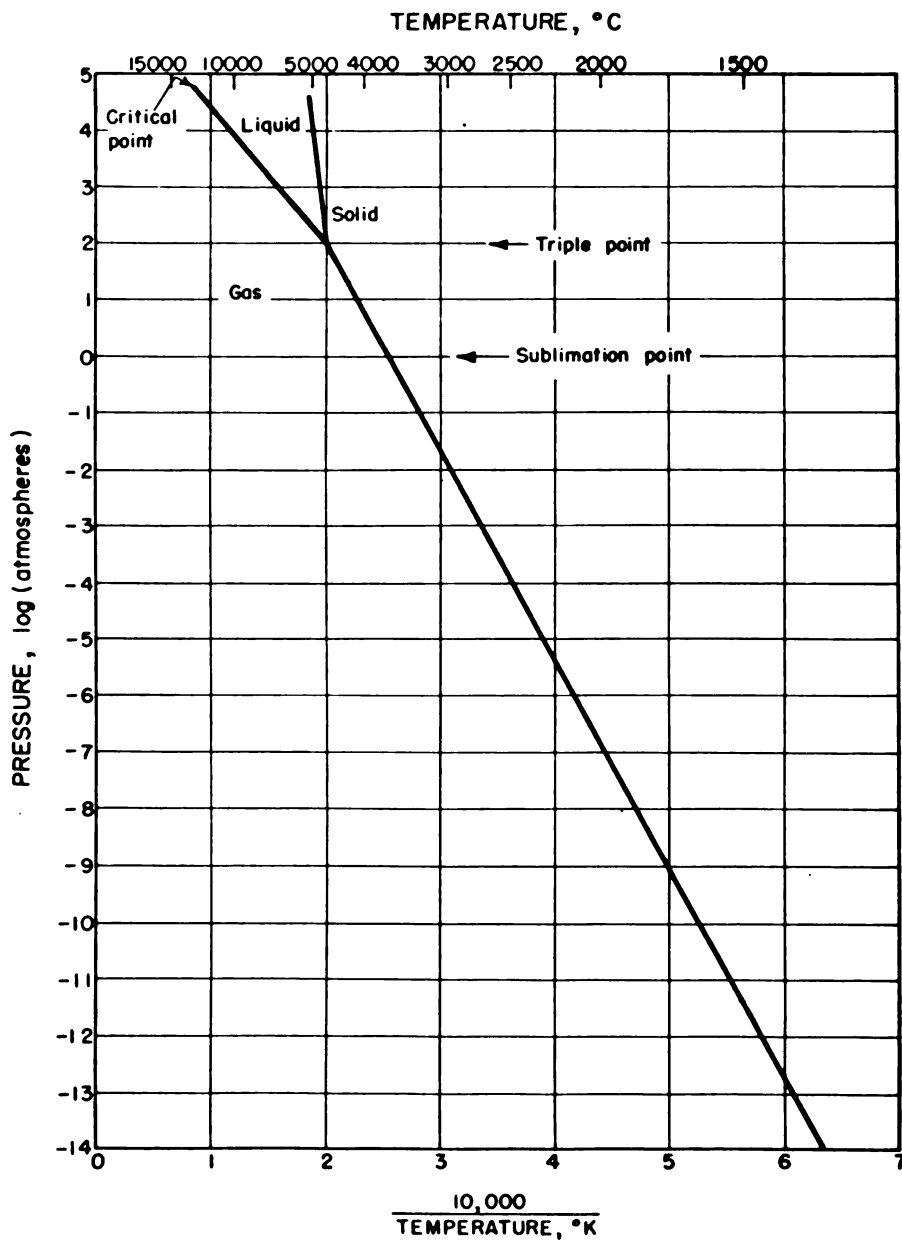


Fig. 1.9.2 — Vapor Pressure of Graphite. Reprinted from M. C. Udy and F. W. Boulger, *The Properties of Graphite*, BMI-T-35, June 20, 1950.

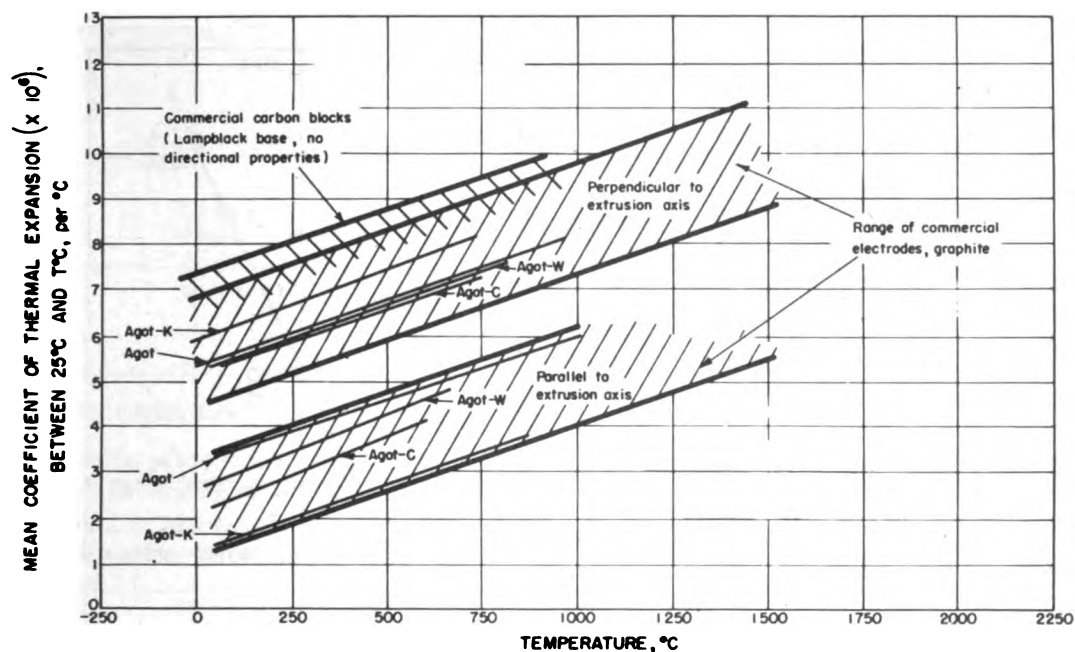


Fig. 1.9.3 — Thermal Expansion Coefficients of Various Graphites. Submitted by Battelle Memorial Institute, Sept. 1, 1952.

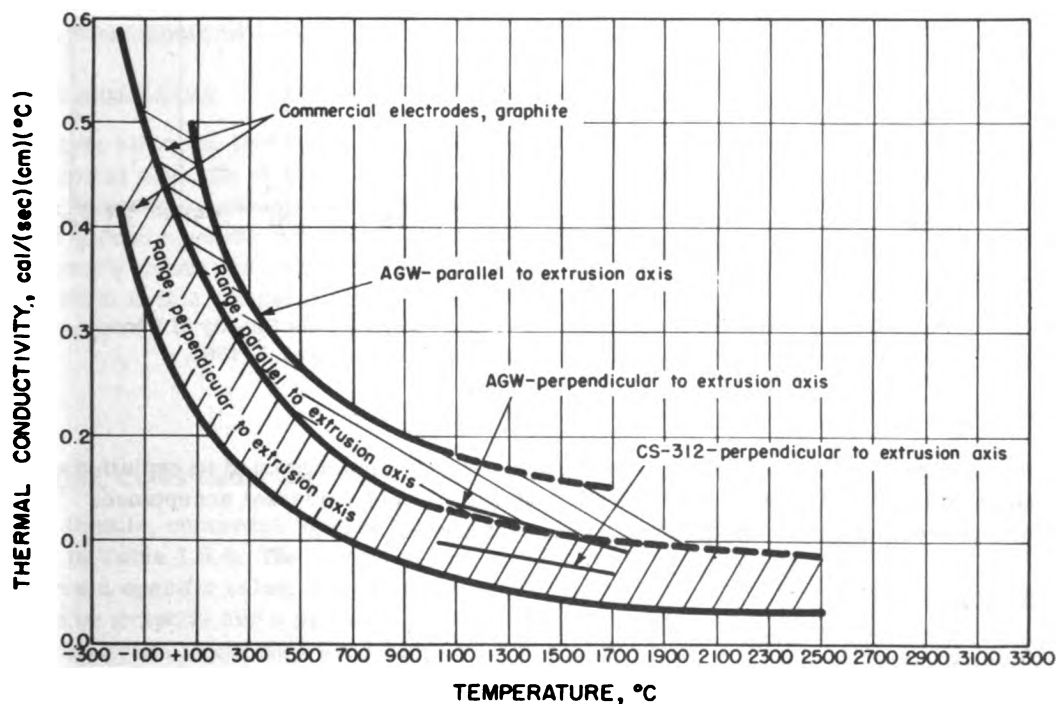


Fig. 1.9.4 — Typical Thermal Conductivities of Various Graphites. Submitted by Battelle Memorial Institute, Sept. 1, 1952.

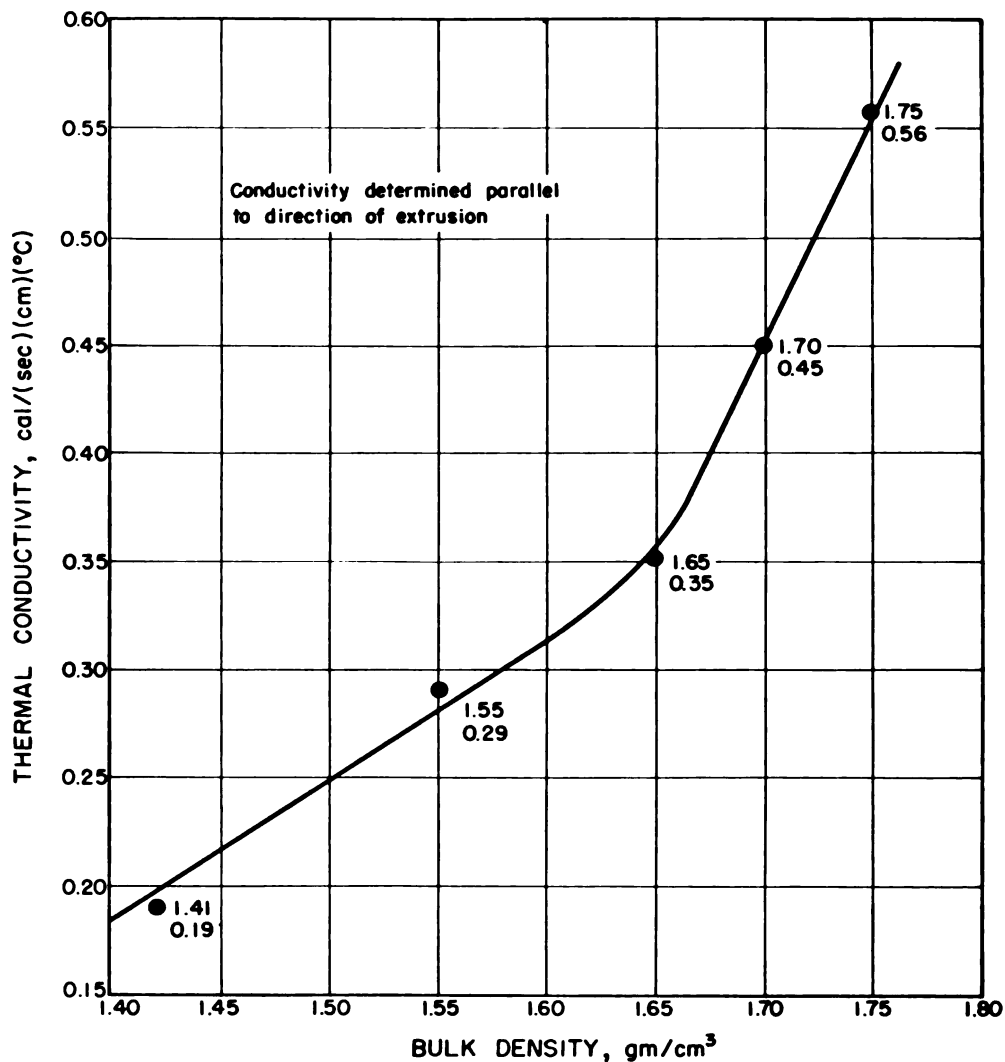


Fig. 1.9.5—Thermal Conductivity of Graphite Versus Bulk Density at Room Temperature. Submitted by Battelle Memorial Institute, Sept. 1, 1952.

repeats the first. Other modifications in structure have been suggested to explain apparent anomalies in diffraction data, but these have not yet met universal acceptance.

The lattice constants for the generally accepted structure are:

$$a_0 = 2.456\text{\AA}$$

$$c_0 = 6.697\text{\AA}$$

$$\text{Bond angle} = 120^\circ$$

The observed spacing for some artificial graphite is shown in Table 1.9.3.

Table 1.9.3 — Lattice Spacings of Artificial Graphite

Type	Spacing, Å	
	a_0	c_0
Commercial electrode (AGX)	2.457 ± 0.002	6.713 ± 0.007
Commercial block (Speer)	2.454 ± 0.002	6.715 ± 0.005
AGOT	2.457 ± 0.002	6.711 ± 0.005
Commercial block (lampblack base)	2.450 ± 0.005	6.77 ± 0.01

HEALTH HAZARDS

No health hazards are known to be involved in handling virgin carbon or graphite. If the material is impregnated with a hazardous substance, care should be exercised, of course, equivalent to that required for the impregnant. Graphite exposed to irradiation requires special handling techniques depending upon the kind and amount of ash and the amount of exposure.

HANDLING AND STORAGE

Finely divided graphite does not present a fire or explosion hazard when dispersed in air. Very-low-temperature carbons (e.g., cokes which have been heated no higher than 400°C) and charcoals do present hazards of this nature and should be handled with the same precautions as high-volatile coals. Owing to the porosity of carbon and graphite, the material should be stored in dry, protected areas. If the material should become wet, precautions should be taken against freezing.

ADSORBED GASES

Oxygen, nitrogen, hydrogen, and/or gaseous sulfur compounds can be pumped from most graphites at absolute pressures in the range of 1 to 5 μ of mercury and at high temperatures. Degassing appears to be complete at 2150°C. The kind and amount of gases so removed depend upon the raw materials and method of processing the graphite. Graphite will absorb about 0.09 weight-percent of water vapor in a saturated atmosphere at 20°C. Absorption at this temperature from an atmosphere of 60-percent relative humidity is negligible.

MECHANICAL PROPERTIES

TENSILE, COMPRESSIVE, AND TRANSVERSE STRENGTH

The tensile, compressive, and transverse strength of carbon and artificial graphite are shown in Table 1.9.4. The values quoted cover a wide range. When the design engineer requires a specific value, the problem should be reviewed with the manufacturer of the carbon or graphite and a product selected for the specific application. The strength of artificial graphite varies with the anisotropic nature of the material and with its bulk density. The relationship between bulk density and tensile strength is illustrated for commercial block graphite in Fig. 1.9.6. Graphite is unique among materials in exhibiting much greater strength at elevated temperatures than at room temperature. This is shown for tensile strength in Fig. 1.9.7. The compressive strength responds similarly with increasing temperature.

Table 1.9.4 — Tensile, Compressive, and Transverse Strengths of Carbon and Artificial Graphite at Room Temperature

Type	Tensile strength, lb/sq in.		Compressive strength, lb/sq in.		Transverse strength, lb/sq in.	
	Longitudinal	Transverse	Longitudinal	Transverse	Longitudinal	Transverse
Commercial electrodes, Carbon	400 to 1,200	...	2,000 to 10,000	...	800 to 6,000	...
Porous carbon	80 to 200	...	3,000 to 900	...	200 to 600	...
Graphite	500 to 2,500	900 to 1,300	3,000 to 4,000	3,000 to 5,000	1,000 to 5,000	...
Porous graphite	50 to 100	...	300 to 500	...	150 to 250	...
Commercial blocks, Carbon	1,000	500 to 3,000	...	2,000 to 8,000	...	1,000 to 4,500
Graphite	500 to 2,000	500 to 3,000	...	3,000 to 6,500	...	1,500 to 4,000
Commercial tubes, Impervious carbon	2,000	...	10,000	...	4,500	...
Impervious graphite	2,500	...	10,000	...	4,500	...
AGOT	2,300	600	1,000 to 2,500	1,000 to 2,000
AGHT						

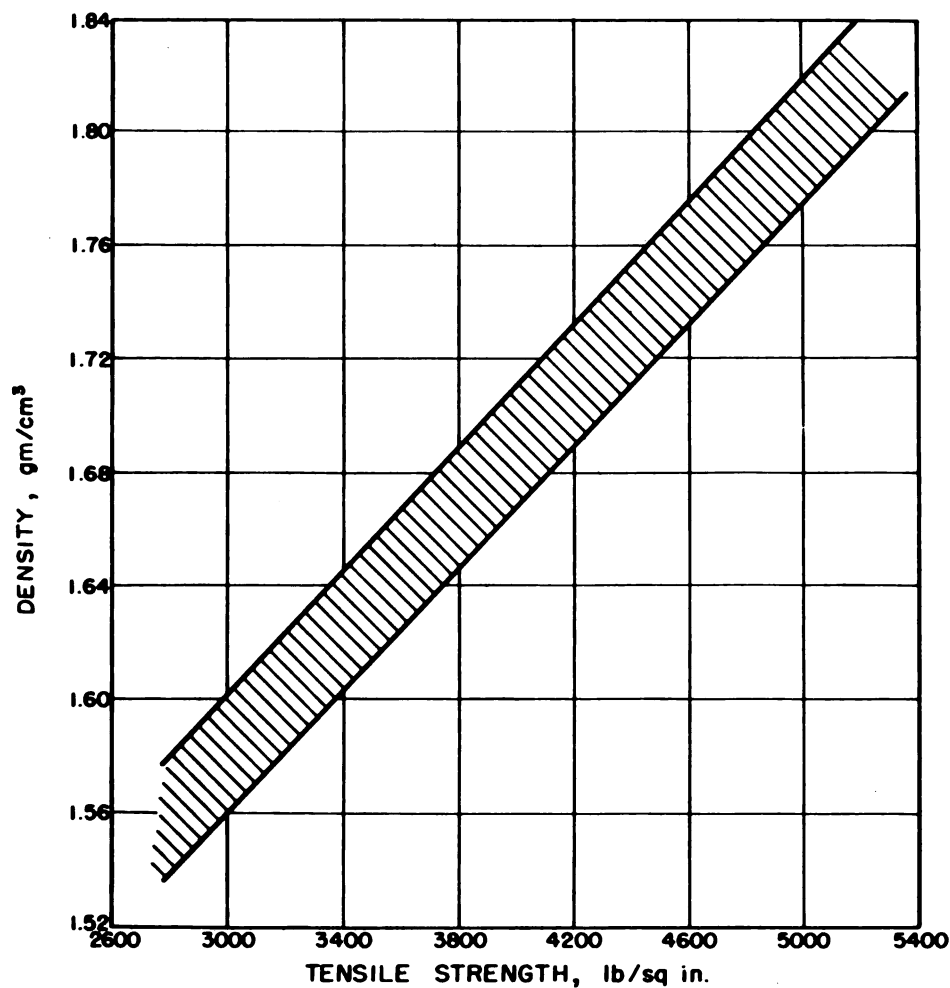


Fig. 1.9.6 — Variation of Room-temperature Tensile Strength With Density for Commercial Block Graphite (EBP). Reprinted from C. F. Malcolm and A. F. Groton, Tensile Strength of Type EBP Graphite at Elevated Temperature and Its Relation to Apparent Density at Room Temperature, NAA-SR-67, Mar. 1950.

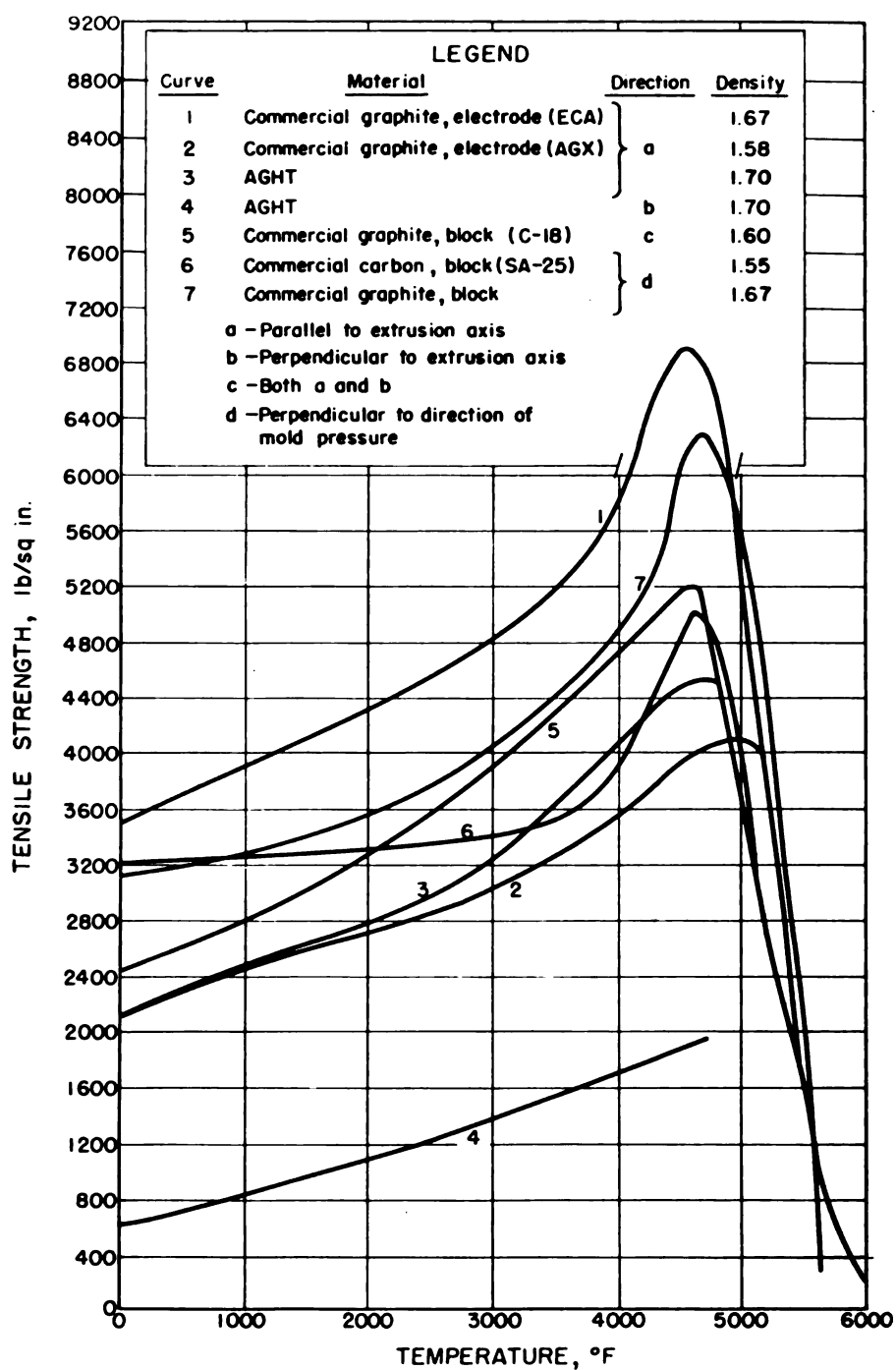


Fig. 1.9.7 —Effect of Temperature on the Tensile Strength of Various Graphites. Reprinted from M. C. Udy and F. W. Boulger, *The Properties of Graphite*, BMI-T-35, June 20, 1950.

MODULUS OF ELASTICITY

The modulus of elasticity of graphite is an anisotropic property. Room-temperature values for carbon and artificial graphite are given in Table 1.9.5. These values were determined on specimens cut with their long axis parallel to the direction of extrusion or perpendicular to the direction of compression molding. The values for graphite are about twice those determined on specimens cut with their long axis perpendicular to the direction of extrusion or parallel to the direction of molding.

Table 1.9.5—Modulus of Elasticity at Room Temperature for Carbon and Artificial Graphite

Type of product	Modulus of elasticity, 10^6 lb/sq in.
Commercial electrodes, carbon	0.5 to 1.4
Commercial electrodes, graphite	0.5 to 1.2
Commercial blocks, carbon	1.1
Commercial blocks, graphite	0.5 to 0.8
Commercial tubes, carbon	1.7 to 2.1
Commercial tubes, carbon, impervious	2.6 to 2.9
Commercial tubes, graphite	1.3 to 1.4
Commercial tubes, graphite, impervious	2.1 to 2.3
Commercial electrodes and blocks, porous	0.12
AGOT	1.4 to 2.1

The temperature dependence of the elastic modulus is shown in Fig. 1.9.8.

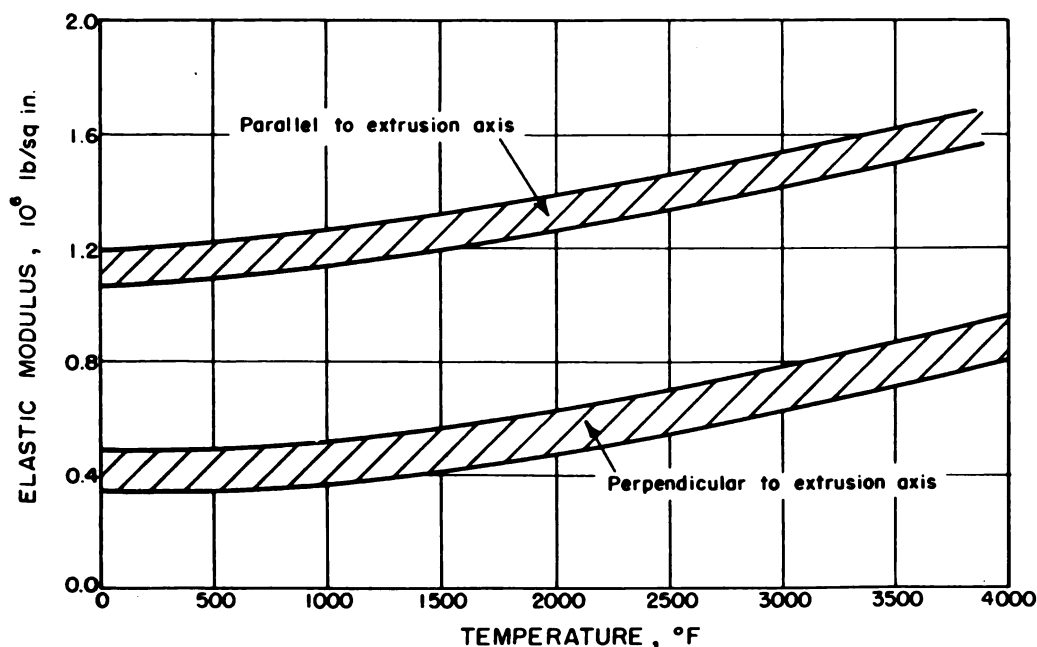


Fig. 1.9.8—Effect of Temperature on the Elastic Modulus of Commercial Electrode Graphite. Adapted from data of L. Green, Jr., Measurement of Young's Modulus of Grade AVF Graphite at Elevated Temperatures, NAA-SR-98, Dec. 7, 1950.

HARDNESS

The hardness of carbon and graphite depends on the raw materials and the method of processing employed in fabrication. Scleroscope hardness values of "less than 25" to "greater than 100" are obtainable. The materials known as "carbon" usually are the harder.

ELONGATION, REDUCTION IN AREA

Poisson's ratio for graphite varies from 0.20 to 0.33. The average value is about 0.25. Examples of elongation and reduction in area of graphite at high temperatures are given in Table 1.9.6.

Table 1.9.6—Ductility of Graphite

Type of graphite	Kind of test	Maximum stress, lb/sq in.	Temperature, °F	Reduction of area, %	Elongation, (2 in. effective gage length), %	Increase in volume, %
AGHT*	Tensile	4380	4800	1.3	7	...
AGHT*	Creep	2200	4800	1.3	9	8
AGHT*	Creep	2800	4320	0.5	2	1
C-18†	Creep	2800	4800	5-7	18	11
C-18†	Tensile	5300	4800	0.4-0.5	18	14
C-18†	Creep	4000	4300	2.7	11	8
C-18†	Creep	2800	4300	1.1	4	3

*Parallel to extrusion direction

†Perpendicular to direction of applied pressure

CREEP

The creep rate at high temperatures of three grades of graphite is shown in Figs. 1.9.9, 1.9.10, and 1.9.11.

FRictional COEFFICIENTS

The coefficients of friction of graphite on itself and on various other materials are shown in Table 1.9.7.

FATIGUE

All surfaces revealed by failure of graphite in fatigue tests both at high and low temperatures are characteristic of brittle fracture. No evidence of fatigue-crack propagation or work hardening is noted. The endurance limit noted in fatigue studies increases with temperature in a manner similar to the short-time tensile strength.

FORMING AND FABRICATION

Carbon and graphite sublime rather than melt; therefore, casting is not possible.

Efforts to sinter or to hot-mold carbon- or graphite-powder compacts so far have not been successful. Evidence indicates that the embryonic crystals of graphite will not grow dependably beyond the domain of the particle of powder.

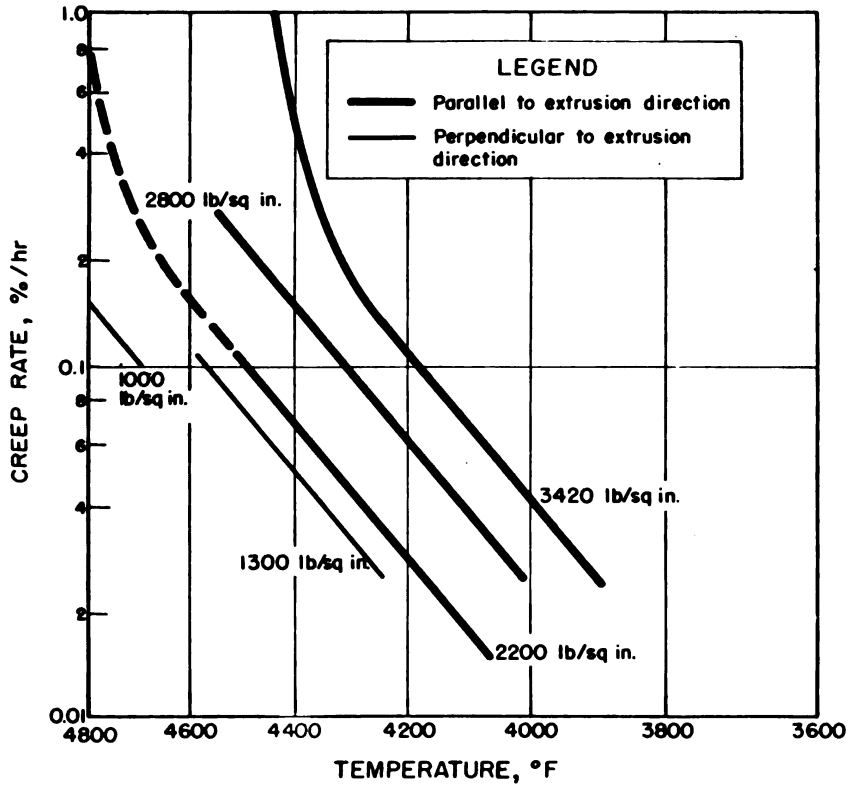


Fig. 1.9.9 — Creep Rate of AGHT Graphite. Reprinted from R. E. Adams and H. R. Nelson, Tensile and Creep Properties of Graphite, NEPA, BMI-N-45, May 1, 1950.

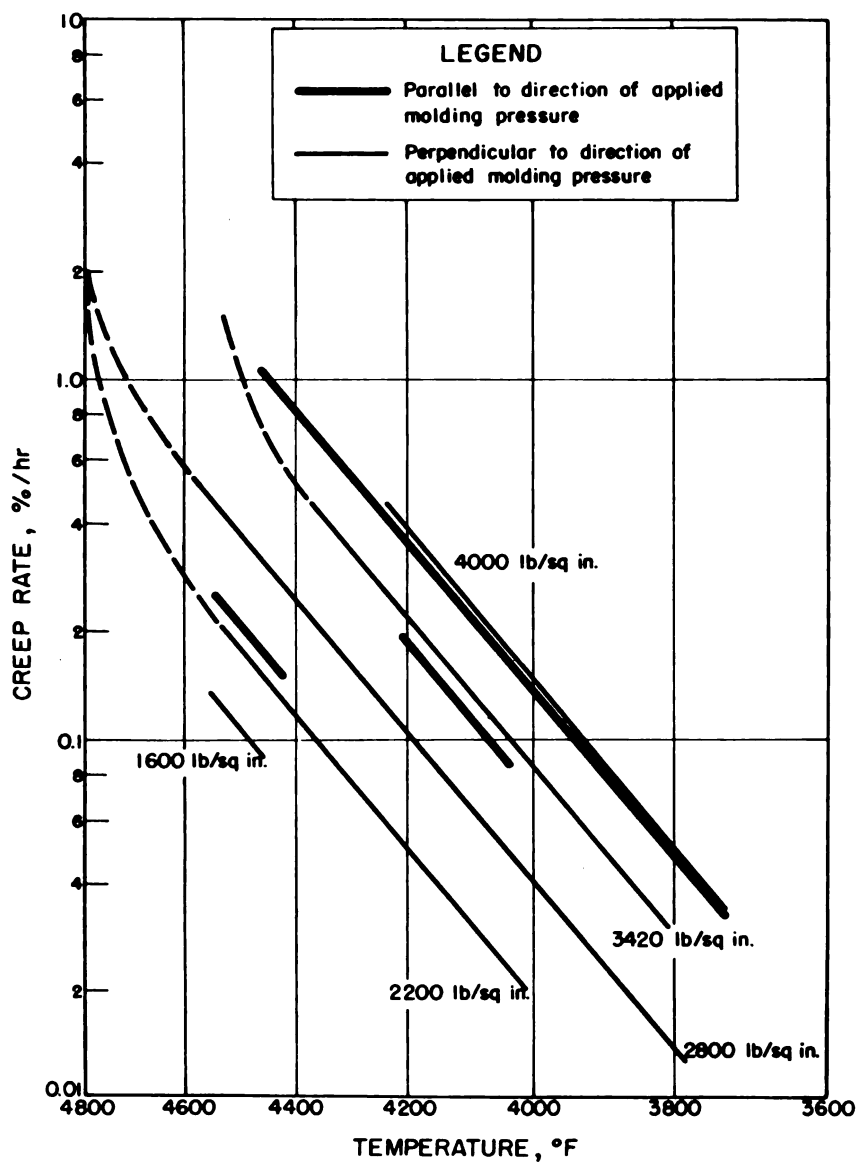


Fig. 1.9.10 — Creep Rate of C-18 Graphite. Reprinted from R. E. Adams and H. R. Nelson, Tensile and Creep Properties of Graphite, NEPA, BMI-N-45, May 1, 1950.

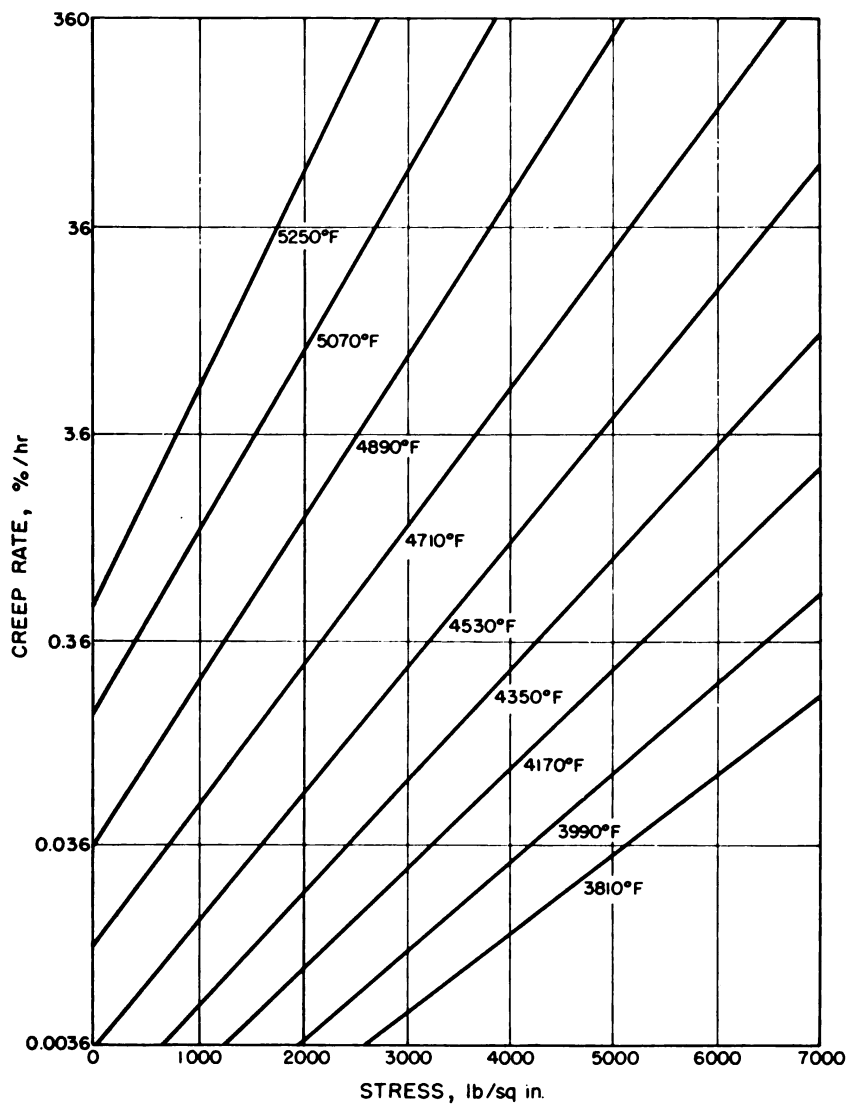


Fig. 1.9.11 — Creep Rate of Commercial Electrode Graphite (ECA). Reprinted from C. F. Malstron, et al., The Creep Characteristics of ECA Graphite, NAA-SR-51, Jan. 26, 1950.

Table 1.9.7—Coefficient of Friction

Materials	Type	Temperature	Coefficient
Graphite on graphite	Static	Room	0.29
Graphite on graphite	Sliding	Room	.22
Oxide-coated uranium on graphite	Static	Room	.56
Oxide-coated uranium on graphite	Sliding	Room	.53
Machined uranium on graphite	Static	Room	.21
Machined uranium on graphite	Sliding	Room	.20
Polished aluminum on graphite	Sliding	Room	.18
Polished aluminum on graphite	Sliding	210°–390°F	.20
Polished 1035 steel on commercial graphite block (Grade ATJ)	Sliding	Room	.36
Polished 1035 steel on commercial carbon block (Grade AOH)	Sliding	Room	.36
Polished 1035 steel on commercial electrode (Grade CK)	Sliding	Room	.22
Polished 1035 steel on AGHT	Sliding	Room	.2

MACHINING

Commercial carbon products are very hard, and, for economical shaping, diamond saws, cutting tools, and wheels should be employed. Where feasible, equipment to receive carbon tubes, electrodes, blocks, and the like should be designed to employ these materials in the shape and size tolerance quoted by the manufacturer, thus essentially eliminating the machining operation.

Commercial-graphite products are relatively soft and can be machined either with wood- or metalworking tools. Band saws containing blades with the fewest teeth per inch are satisfactory for rough shaping. Hollow drills connected to a source of vacuum for dust removal are more successful than ordinary twist drills for drilling and boring. For lathe work, a 4-jaw chuck is better than a 3-jaw chuck to receive the frequently out-of-round electrodes. For a rough lathe finish, the depth of the cut may be as great as 0.5 in. and the rate of feed as fast as 0.1 in./rev. For a semifine finish, the rate of feed should be reduced to 0.02 to 0.05 in./rev. A tolerance of ± 0.003 in. can be maintained on this operation. For a fine finish, the depth of cut varies from 0.001 to 0.1 in. and the rate of feed from 0.005 to 0.02 in./rev. In this machining, a tolerance of ± 0.002 in. can be maintained.

In milling operations, the life of a tungsten carbide cutting tool is shorter than that of the same cutter on ordinary steel. The wear on the cutters is the same on the first three pieces as on the next one hundred.

JOINING

True welding of carbon or graphite to carbon or graphite, with carbon or graphite as the weld material, has not been accomplished, probably for the reasons cited under powder metallurgy.

Graphite may be joined to graphite with molybdenum disilicide as the weld material. The assembly must be heated to about 3900°F to produce the weld. Assemblies so joined are gas tight and are serviceable to about 3500°F. Other metals may be employed as the weld material, and reputedly, conventional soldering techniques may be employed if the graphite surfaces to be joined are converted first to a carbide, for example, of molybdenum or tungsten to promote the wetting of the graphite by the molten metal.

Carbon or graphite bricks or blocks, when employed to line processing containers, are laid with proprietary carbon-paste mortars. These mortars usually are mixtures of powdered coke or graphite and asphalt or pitch diluted with a suitable solvent. Some are acid-resistant. None join the carbon or graphite blocks in any sense other than a lime or cement mortar joins clay bricks or blocks.

HEAT TREATMENT

RECRYSTALLIZATION AND GRAIN GROWTH

Graphite crystals reputedly do not grow across boundaries established in the raw materials. Recrystallization within the boundaries proceeds at a measurable rate at 3810°F. This rate increases with temperature, so that commercial processes for graphitization (recrystallization) are economically feasible at temperatures in the range of 4170° to 4530°F.

THERMAL SHOCK RESISTANCE

Commercial graphite tubes (KS grade), 12 in. long and varying from $\frac{3}{16}$ -in. ID \times $\frac{3}{4}$ -in. OD to $\frac{1}{16}$ -in. ID \times 1-in. OD, withstood a radial power throughput of 5.2 Btu/(cu in.)(sec) without failure. This is equivalent, in the case of the tube having a wall thickness of $\frac{15}{32}$ in., to 1.3 Btu/(sec)(sq in. of heat-transfer surface). Commercial graphite electrodes employed in electric steel furnaces frequently are pulled rapidly from the furnace while at operating temperature (3000°F). None spall from thermal shock, although cracks develop sometimes on the surface of the electrode, owing to the thermal stress. The calculated radial power throughput of an electrode 18 in. in diameter (a hypothetical tube having a wall thickness of 9 in.), during the first minute of cooling, is 0.8 Btu/(sec)(sq in. of heat-transfer surface).

CORROSION BEHAVIOR

The reaction of graphite with various gases, aqueous solutions, and solids is shown in Table 1.9.8.

PROTECTIVE TECHNIQUES

Numerous processes have been proposed for the application of protective coatings on carbon and graphite. Owing to the inability of the coatings to provide long-time protection, none are in commercial use. All probably provide some protection for a limited time.

Most attention has been given to the problem of protecting graphite against oxidation at high temperatures. Two approaches have been employed: (1) the direct application of a metal or ceramic coating to the surface of the graphite shape, and (2) the dispersion throughout the graphite body of a metal and/or ceramic material which forms a protective surface film when the body is subjected to oxidizing service conditions (a small amount of graphite is "lost" from the surface as carbon dioxide before the film develops).

Examples of applied coatings are silicon carbide, molybdenum disilicide, chromium, nickel, and nickel coated with refractory enamels. Graphites coated with silicon carbide or molybdenum disilicide appear to have lives of 50 to 100 hr at temperatures near 2725°F.

Examples of materials incorporated in the graphite body to provide a protective film during use are ferromanganese-silicon alloys, silicon carbide and manganese-silicon

Table 1.9.8 — Reaction of Graphite With Corrosive Agents

Agent	Temperature, °F	Effect or product
Gases		
Oxygen	840* and higher	Produces carbon oxides
Hydrogen	1650 to 1830	Methane (catalyst necessary)
	3630 and higher	Acetylene (traces)?
Fluorine	1650 to 3450	Produces carbon fluorides
	Room temperature	Interlamellar compounds
Bromine	Room temperature	Interlamellar compounds
Potassium vapor	Room temperature	Interlamellar compounds
Nitrogen	Up to 5430	No effect
Water vapor	1470 and lower	Negligible reaction
	1470 and higher	Increasingly severe attack
Chlorine	Up to 4170	No effect
Carbon dioxide	1470 and lower	Negligible reaction
	1470 and higher	Carbon monoxide
Aqueous solutions		
Dilute acid or alkali	Less than boiling	No attack
Strong acid (HNO ₃ and H ₂ SO ₄)	570 and higher	Graphitic oxide
KOH (50% solution)	660 and higher	Dissolves graphite
Solids		
Alkali hydroxides (inert atmos.)	At fusion	No attack
Sodium sulfate	At fusion	No attack
Sodium carbonate	At fusion	Carbon monoxide
Metals (most)	2730 and higher	Metal carbide
Metal oxides	2730 and higher	Metal carbide and carbon oxides

*Attack at 660°F is reported; the weight loss is not measurable, but a slight, permanent increase in length is noted

alloys, and silicon carbide and aluminum. Coatings obtained in this manner provide protection at temperatures up to about 2730°F for variable periods of time. When the coating fails, additional graphite is oxidized, exposes additional coating material which fuses and thus provides a new coating. Graphite shapes which must retain constant dimensions during use cannot be protected in this manner.

CRUCIBLES AND MOLDS

The extreme refractoriness, the excellent resistance to thermal shock, and the resistance to wetting by most molten substances make graphite a suitable material for crucibles and molds in many instances. Also, graphite serves as a susceptor for induction heating; thus, the crucible or mold may serve a dual purpose.

The solubility of carbon in molten vanadium, uranium, thorium, zirconium, and titanium, in particular, discourages rigorous melting of these particular metals in graphite crucibles. The time of contact between the molten metal and the crucible should be as short as possible. When used, care should be exercised in selecting graphite for this service; the ash content should be as low as possible (at least equal to AGOT), and the crucible should be cut from the electrode so that the axis is parallel to the axis of extrusion. Only fine-grained stock should be selected. The electrode diameter preferably should be no larger than that necessary to obtain the desired crucible as the fineness of the grain usually decreases with decreasing electrode diameter. Molded stock is less desirable for crucibles and molds; if used, the crucible should be cut with its axis perpendicular to the direction of molding (usually the shortest dimension of the block).

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CHAPTER 1.10

Hydrides

M. W. Mallett and V. M. Shepline

Because the metal hydrides dissociate into the metal and free hydrogen on heating, several of them are useful as a source of hydrogen of high purity. They are also used in the production of metal powders and alloys of metals which are difficult to prepare by other methods. The safe and easy handling of the more stable metal hydrides makes possible numerous other laboratory and metallurgical applications. For example, hydrides are used as reducing and condensing agents, analytical reagents, dry agents, and as fluxes in brazing operations. A few of these uses are discussed later under the appropriate hydrides.

REACTOR APPLICATION

Extensive studies have been made on the production of a suitable hydrogenous material for use with a nuclear reactor, either as a moderator or as a radiation shield. Hydrides of the heavy metals are of particular interest in the latter respect. The combination of hydrogen with a heavy metal as a hydride would afford high gamma absorption as well as good neutron attenuation. Thus the best hydride for shielding purposes should have a maximum hydrogen content and high density and should be a solid that is stable in the higher temperature regions.

Any hydride used as a radiation shield must have a container impervious to hydrogen and capable of withstanding relatively high pressure. Such containers must resist attack by the hydrides at high temperature, must have high tensile strength, and must be sealed hermetically without introduction of air or decomposition of the contents. It is estimated that the tensile strength should be about 50,000 lb/sq in. at 1200°F. Low-carbon stainless steels and Nichrome are suitable and easily available materials for use as containers. Little attention has been given to materials not readily available in tube form because of the time and expense required for their fabrication.

Some hydrides are not stable much above room temperature, but large amounts of hydrogen might be held in loose combination with the metal in a sealed briquette. Satisfactory canning techniques have not as yet been fully developed for preparing the hydrides for shielding purposes. This and other important factors affecting the reactor application of hydrides are still undergoing intensive investigation.

PHYSICAL AND CHEMICAL CONSTANTS

The available data have been classified for presentation in the following order: borohydrides, alkali-metal hydrides, alkaline-earth metal hydrides, complex aluminum hydrides,

and heavy-metal hydrides. The decomposition-pressure isotherms have been grouped to afford easier comparison.

BOROHYDRIDES

Gaseous hydrides (M_xH_y) are formed by boron and the elements of the main Groups IV through VII of the periodic chart. Because gaseous hydrides appear to have no present application to reactor design, they are not discussed here.

The borohydrides [$M_x(BH_4)_y$] are relatively stable liquids and solids. They are white or colorless crystals usually prepared by reacting diborane, B_2H_6 , with a methyl- or ethyl-metal derivative. $Th(BH_4)_4$ has been prepared by reacting anhydrous thorium tetrafluoride with aluminum borohydride. The existence of $Ti(BH_4)_3$, $U(BH_4)_3$, $Pu(BH_4)_3$, $Hf(BH_4)_4$, and $Np(BH_4)_4$ has been reported. Attempts are being made to prepare tungsten borohydrides. The borohydride of gallium, $Ga(BH_4)_3$, may form as an intermediate but decomposes rapidly. Volatile methylated borohydrides have also been isolated. Table 1.10.1 lists selected chemical and physical properties of some of the borohydrides.

ALKALI-METAL HYDRIDES

All alkali-metal hydrides are white and have a face-centered cubic (NaCl) crystal structure. They are strong reducing agents. Some of these hydrides have good thermal stability. However, the hydrogen concentration is rather low compared with that of the hydrides of heavier metals. They are insoluble in organic solvents, but NaH is soluble in molten metals. Most of these hydrides conduct electricity in the molten state. They decompose in water and acids and are relatively stable at high temperatures if excess metal is present. NaH ignites in oxygen at 230°C and burns with other oxidizing agents. In the absence of moisture, LiH is not reactive with oxygen, chlorine, or hydrogen chloride vapors. Each of the alkali-metal hydrides is attacked by carbon dioxide and sulfur dioxide, producing the formate and the hydrosulfite, respectively. Some properties of alkali-metal hydrides are given in Table 1.10.2.

ALKALINE-EARTH METAL HYDRIDES

Elements of Group II form relatively stable hydrides which are white to gray-white crystals, insoluble in most solvents, and readily decomposed in water and acids. The hydrides of strontium and barium are attacked by nitrogen above a red heat. SrH_2 also reacts with oxygen, sulfur dioxide, and the halogen vapors. BeH_2 reacts very slowly with dry air at room temperature.

CaH_2 has good thermal stability and is easily handled. It is used extensively as a reducing agent in the production of pure metals and as a drying agent, condensing agent, and portable source of hydrogen. It may also be used to determine traces of water in organic solvents.

Radium hydride has not been prepared, but it should have a heat of formation of about 35 kcal and a dissociation temperature of 900°C and should evolve about 55 kcal upon reacting with water.

Data on the hydrides of beryllium, magnesium, calcium, strontium, and barium are summarized in Table 1.10.3. The last three hydrides listed in Table 1.10.3 have orthorhombic structures.

COMPLEX ALUMINUM HYDRIDES

The aluminohydrides are generally prepared by reacting the metal hydride with $AlBr_3$ in dimethyl ether. $Mg(AlH_4)_2$ is also produced when lithium-aluminum hydride reacts with magnesium bromide or Grignard reagent, $MgRX$. White crystals of AlH_3 form at 100 to

Table 1.10.1—Some Physical and Chemical Properties of the Borohydrides

Borohydride	Density, gm/cm ³	10 ²² H atoms/cm ³	Melting point, °C	Boiling point, °C	Vapor pressure at 0°C, mm	ΔH_f° , kcal/mole	Crystal structure	Lattice constants, Å	Reactivity
Aluminum, (s)* Al(BH ₄) ₃	0.544†	5.55	-84.5	44.5	119.5	7.16	Reacts readily with air; hydrolyzes rapidly at room temperature; reacts with HCl, O ₂ , H ₂ O, NH ₃ and tri- methylamine
Beryllium, (s) Be(BH ₄) ₂	123	91.3	0.5	14.81	Burns violently in air; reacts vigorously with H ₂ O, HCl, and trimethylamine
Decaborane, (s) B ₁₀ H ₁₄	0.94-0.96†	6.58	99.6	213	...	8	Two symmetrical pentagons bonded by B-B	a ₀ = 14.49 b ₀ = 20.89 c ₀ = 5.70	Reacts vigorously with air at 100°C
Lithium, (s) LiBH ₄	0.681	7.34	275	Decomposes >275	<10 ⁻⁶	-44.6	Orthorhombic	a ₀ = 6.82 b ₀ = 4.44 c ₀ = 7.72	Stable at 90°C in vacuo; very reactive to moisture; very stable in dry air; reacts with HCl and CH ₃ OH
Magnesium, (s) Mg(BH ₄) ₂	Reacts with CH ₃ OH at room temperature
Sodium, (s), NaBH ₄	1.074	6.94	...	Decomposes >300	...	-43.82	Face-centered cubic	a ₀ = 6.163	Stable under normal atmosphere condi- tions; does not react with cold water; re- active to moist air
Thorium, (s) Th(BH ₄) ₄	2.59	8.62	Stable indefinitely in H ₂ below 150°C; decom- poses slowly in air; soluble in tetrahydro- furan and diethylamine
Zirconium, (s) Zr(BH ₄) ₄	1.185†	7.64	Cubic	a ₀ = 5.953	...

*(s) = solid or condensed phase

† Nominal X-ray density

Table 1.10.2—Some Physical and Chemical Properties of Alkali-metal Hydrides

Hydride	Density, gm/cm ³	10 ²³ H atoms/cm ³	Melting point,* °C	$\Delta H_{\text{f,hyd}}^0$, kcal/mole	$\Delta F_{\text{f,hyd}}^0$, kcal/mole	$\Delta S_{\text{f,hyd}}^0$, cal/(mole)(°C)	Lattice constant, A	Preparation
Lithium, (s)† LiH	0.82	6.32	680	-21.61	-16.72	-16.4	4.085	Li + H ₂ below 710°C; ether solutions of methyl lithium and lithium-aluminum hydride
Sodium, (s) NaH	1.36-1.396	3.40	Decomposes at 430	-13.7	-9.3	-14.8	4.96	Na + H ₂ at 350-360°C
Potassium, (s) KH	1.43-1.47	2.16	Decomposes at 430	-13.6	-8.9	-15.6	5.70	K + H ₂ at 350°C
Rubidium, (s) RbH	2.59	1.82	Decomposes at 300	-12.00	-7.3	-15.8	6.03	Heating the carbonate with Mg at 650°C in H ₂ atm; Rb + H ₂ at 350°C
Cesium, (s) CsH	3.41	1.54	Decomposes	-12.00	-7.3	-15.8	6.37	Heating the carbonate with Mg at 580-620°C in H ₂ ; Cs + H ₂ at 300°C

*Decomposition temperatures below the melting point are given at a hydrogen pressure of 1 atm

†(s) = solid or condensed phase

Table 1.10.3—Some Chemical and Physical Properties of the Alkaline-earth Metal Hydrides

Hydride	Density, gm/cm ³	10 ²² H atoms/cm ³	Melting point,* °C	$\Delta H_{\text{f,hyd}}^0$, kcal/mole	$\Delta F_{\text{f,hyd}}^0$, kcal/mole	$\Delta S_{\text{f,hyd}}^0$, cal/(mole)(°C)	Lattice constants, A	Preparation
Beryllium, (s)† BeH ₂	Decomposes at ~125	Treating dimethylberyllium with lithium-aluminum hydride in diethyl ether in vacuo at 25°C
Magnesium, (s) MgH ₂	Decomposes at 280-300	Treating ethereal solution of diethylmagnesium with ether solution of lithium-aluminum hydride or diborane; use of Grignard reagent, MgRX
Calcium, (s) CaH ₂	1.9	4.9	Decomposes at 900	-45.1	-35.8	-31.2	a ₀ = 5.936 b ₀ = 6.838 c ₀ = 3.600	Ca + H ₂ at 400-500°C; reducing CaO with zinc in H ₂ ; electrical fusion of lime in H ₂
Strontium, (s) SrH ₂	3.27	4.43	650	-42.3	-32.8	-31.9	a ₀ = 6.364 b ₀ = 7.343 c ₀ = 3.875	Reducing SrO with zinc in H ₂ ; heating Sr-Cd alloy with SrO to red heat in H ₂ atmosphere
Barium, (s) BaH ₂	4.21	3.66	Decomposes at 725	-40.9	-31.5	-31.5	a ₀ = 6.768 b ₀ = 7.829 c ₀ = 4.167	Ba + H ₂ at 600°C; H ₂ acting on barium amalgam at high temperatures

*Decomposition temperatures below the melting point are given at a hydrogen pressure of 1 atm

†(s) = solid or condensed phase

135°C from trimethylaluminum in trimethylamine. Both sodium- and lithium-aluminum hydrides can be used as reducing agents for organic compounds and also as color tests for the presence of aromatic nitro, aromatic nitroso, and azoxy compounds. NaAlH_4 starts decomposing when it melts at 180 to 190°C. LiAlH_4 ignites in air at 130°C and melts with decomposition at 150°C on rapid heating. Its density is 0.943 gm/cm³. Table 1.10.4 lists the solubility and reactivity of some complex hydrides of aluminum.

Table 1.10.4—Some Properties of Complex Hydrides of Aluminum

Hydride	Solubility	Reactivity
Aluminum, AlH_3	Partly soluble in dimethyl Cellosolve and dimethyl ether	Highly explosive in presence of AlCl_3 and residual ethers; reacts slowly with NaH in presence of tetrahydro- furan
Lithium aluminum, LiAlH_4	Soluble in pure dimethyl ether (with caution)	Moderately stable in dry air at room temperature; explosive if dissolved in impure dimethyl ether; reacts with trimethylboron at room tem- perature; reacts violently with water
Magnesium aluminum, $\text{Mg}(\text{AlH}_4)_2$...	Reacts with water and acetone
Sodium aluminum, NaAlH_4	Slightly soluble or insoluble in diethyl ether	Reacts rapidly and completely with H_2O and NH_3 ; reacts with BCl_3 in diethyl ether

HEAVY-METAL HYDRIDES

The principal chemical and physical data on the heavy-metal hydrides are given in Tables 1.10.5 and 1.10.6.

DECOMPOSITION-PRESSURE ISOTHERMS

Figures 1.10.1 to 1.10.7 show the decomposition-pressure isotherms for the systems calcium-, niobium-, palladium-, plutonium-, titanium-, thorium-, and zirconium-hydrogen. Figure 1.10.8 gives the hydrogen pressure-temperature relations for the hydrides of uranium, sodium, and potassium. Figure 1.10.9 gives the hydrogen pressure-temperature relations for the hydrides of barium, lithium, calcium, and strontium.

It is obvious from these isotherms that in many cases the dissociation pressure varies with the hydrogen content of the hydride. In a few cases (LiH , SrH_2 , and BaH_2 in Fig. 1.10.9) where this variation appears to occur, the pressure-composition data are incomplete; therefore, only the dissociation pressures at stoichiometric composition were plotted. Still other hydrides apparently are not affected by the over-all hydrogen composition of the system (Fig. 1.10.8).

In some hydrogen-metal systems, such as that of hydrogen and palladium, marked hysteresis effects between the absorption and evolution isotherms are noted. The evolution curves only were plotted in such cases.

Table 1.10.5—Some Chemical and Physical Properties of Heavy-metal Hydrides*

Hydride	Color	Density, gm/cm ³	10 ²³ H atoms/cm ³	ΔH_{298}° , kcal/mole	ΔF_{298}° , kcal/mole	ΔS_{298}° , cal/(mole)(°C)	Crystal structure	Lattice constants, Å	
								a_0	c_0
Cadmium (s)†	White								
...									
Cerium, (s)	Dark blue	5.5	7.0	-42.26	Amorphous
CeH ₃									
Chromium, (s)	White	6.22†	7.12	Hexagonal, close packed	2.72	4.42
CrH									
CrH ₂ or CrH ₃ , actual com- position un- certain	Black	6.76	22.4	-3.80	Face-centered cubic	3.8605	...
Copper, (s)	Reddish brown to black	6.38	6.00	+5.12	Hexagonal, close packed (zincite)	2.893	4.614
CuH									
Hafnium, (s)	Tetragonal
HfH ₂									
Lanthanum, (s)	Bluish black	5.26	6.73	-40.09	Amorphous
LaH ₃									
Neodymium, (s)	Indigo blue	Amorphous
NdH ₂									
Nickel, (s)	...	7.04	14.0	Hexagonal	2.684	4.382
NiH ₂									
Niobium, (s)	Gray	6.0-6.6	3.87-4.26
NbH									
Palladium, (s)	Metallic	10.76	5.75	-9.28	Face-centered cubic	3.978-4.036	...
Pd ₂ H									
Plutonium, (s)	-32.5
PuH ₂									
PuH ₃	-37.0
Praseodymium, (s)	Green	5.5	7.0	-39.5	Amorphous
PrH ₃									
Tantalum, (s)									
Ta ₂ H		14.72†	2.47	Hexagonal, close packed	3.09	4.92
TaH	Black	15.25†	5.08	Orthorhombic	4.81 ($b_0 = 4.78$)	3.43

Table 1.10.5—(Continued)

Hydride	Color	Density, gm/cm ³	10 ²² H atoms/cm ³	ΔH_{298}° , kcal/mole	ΔF_{298}° , kcal/mole	ΔS_{298}° , cal/(mole)(°C)	Crystal structure	Lattice constants, Å	
								a_0	c_0
Thorium, (s) ThH ₂	Greenish gray to black	9.20	4.77	-35.20	Body-centered tetragonal	4.10	5.03
ThH ₄	Black	8.25	8.48	-43	-24.4	-62.5	Body-centered cubic	9.11	...
Titanium, (s) TiH		3.79†	4.69	Face-centered cubic	4.40	...
TiH ₂	Dark gray	3.912	9.52	-5.168	-0.709	-14.96	Face-centered cubic (CaF ₂)	4.45	...
Uranium, (s) UH ₃	Brownish gray to brownish black	10.92	8.27	-30.4	-17.7	-42.6	Simple cubic	6.634	...
Vanadium, (s) probably VH ₃	...	5.30	16.2
Zinc, (s) ZnH ₂	White
Zirconium, (s) ZrH	...	5.96†	0.99	Face-centered cubic	4.67	...
Zr ₂ H	...	5.74†	1.89	Hexagonal, close packed	3.35	5.46
ZrH	...	5.61†	3.69	Face-centered cubic	4.78	...
ZrH ₂	Dark gray	5.625†	7.38	-40.5	Face-centered tetragonal identical with tetragonal body-centered	4.974	4.449
								3.520	4.449

*See also Table 1.10.6
†(s) = solid or condensed phase
‡Nominal X-ray density

Table 1.10.6—Reactivity, Stability, and Preparation of Heavy-metal Hydrides

Hydride	Reactivity	Stability	Preparation
Cadmium	Very unstable; decomposes rapidly at about 0°C	Dimethylcadmium in ether + LiAlH_4 at -76.5°C
Cerium, CeH_3	Reacts with ThS_2 , CeS_3	Stable at 1000°C at 1 atm	$\text{Ce} + \text{H}_2$ at 1 atm $< 100^\circ\text{C}$ CeO_2 heated in H_2 $\text{Ce} + \text{H}_2$ at $250-270^\circ\text{C}$
Chromium, CrH	...	May decompose to body-centered cubic metal spontaneously in air	Electrodeposited from chromic acid solution at 12°C
$\text{CrH}_2-\text{CrH}_3$...	Not stable much above room temperature; decomposes to body-centered cubic metal when heated	Electrodeposited from chromic acid solution $< 8^\circ\text{C}$
Copper, CuH	Ignites in Cl_2 ; reacts with HCl	Very unstable; decomposes suddenly at 80°C ; water and other liquids have a stabilizing effect	Sodium hypophosphite + dilute cupric sulfate at 70°C
Hafnium, HfH_2	Not hygroscopic	Stable at room temperature	$\text{Hf} + \text{H}_2$ at 800°C
Lanthanum, LaH_3	...	Stable to 1000°C at 1 atm	$\text{La} + \text{H}_2$ at $220-270^\circ\text{C}$
Neodymium, NdH_2	...	Stable to 1000°C at 1 atm	$\text{Nd} + \text{H}_2$ at $220-270^\circ\text{C}$
Nickel, NiH_2	...	Not stable much above room temperature	Partial success with attempts to hydride spongy Ni at 700–800 psi
Niobium, NbH	Not attacked by acids	Burns readily in air	Nb heated with H_2
Palladium, Pd_3H	Not hygroscopic	Evolves H_2 in vacuo at 100°C ; stable to 80°C	$\text{Pd} + \text{H}_2$ at $80-180^\circ\text{C}$ or higher; electrolysis of dilute H_2SO_4 using Pd cathode

Table 1.10.6 — (Continued)

Hydride	Reactivity	Stability	Preparation
Plutonium, PuH ₂	...	Stable at room temperature in H ₂ at 350 mm Hg	Pu + H ₂ at 585 mm and 24–50°C
Praseodymium, PrH ₃	...	Stable to 1000°C at 1 atm	Pr + H ₂ at 220–270°C
Tantalum, TaH	Not hygroscopic	Stable at room temperature	Ta ₂ O ₅ reduced by CaH ₂ ; Ta + H ₂ at 1000°C; electrolysis at 25°C
Thorium, ThH ₂	Reacts with H ₂ S, ThS ₂ , Ce ₂ S ₃	Readily oxidizes; ignites in air at 260°C	Th + H ₂ above 200°C > $\frac{1}{2}$ atm
ThH ₄	Reacts with HCl, Cl ₂ , HBr, Br ₂ , HF, HI, PH ₃ , H ₂ S, H ₂ O gases	Pyrophoric; stable in CO ₂ to 350°C; decomposes at 400°C in vacuo	Th + H ₂ at 350–400°C
Titanium, TiH ₂	Powerful reducing agent	Ignites in air at 440°C; not appreciably reactive with water or weak acid	Ti + H ₂ ; TiO ₂ reduced at 900–1000°C with Zn or CaH ₂ in H ₂ atmosphere
Uranium, UH ₃	Reacts with gases, aqueous acids and bases, halogenated organic solvents, oxidants, water; pyridine, aniline, and triethylamine vapor treatments reduce pyrophoricity	Pyrophoric in air; safe in CO ₂ and N ₂ to 200–224°C; stable below 420°C at 1 mm H ₂ ; decomposes at 436°C at 1 atm H ₂	U + steam at 250°C; U + decalin or tetralin at 210–270°C; U + H ₂ at 225–300°C > $\frac{1}{2}$ atm
Zinc, ZnH ₂	Reacts slowly with H ₂ O; absorbs diborane in ether	Decomposes slightly in air at room temperature	Dimethylzinc + diethyl ether solution of LiAlH ₄ ; dimethylzinc + dimethylaluminum hydride
Zirconium, ZrH ₂	Reacts with oxidizing agents at high temperature; good "gettering" agent	Ignites in air at 430°C; stable in air, H ₂ O, H ₂ , and inert gases at normal temperature; can be dried in air at 100°C	ZrO ₂ reduced with CaH ₂ , Ca, Zn, Mg, or Si in H ₂ atm; Zr + H ₂ ; ZrCl ₃ + LiAlH ₄ in ether; Zr halide + alkyl Grignard in presence of H ₂

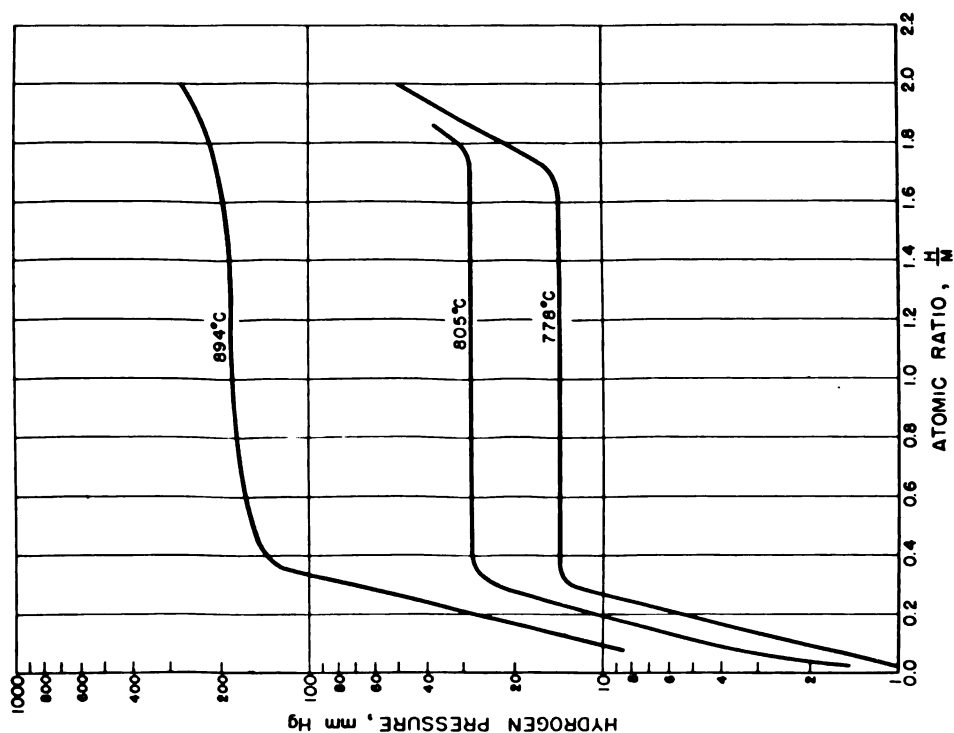


Fig. 1.10.1 — The Decomposition-pressure Isotherm for the System Calcium-Hydrogen. Submitted by Battelle Memorial Institute, May 1, 1952.

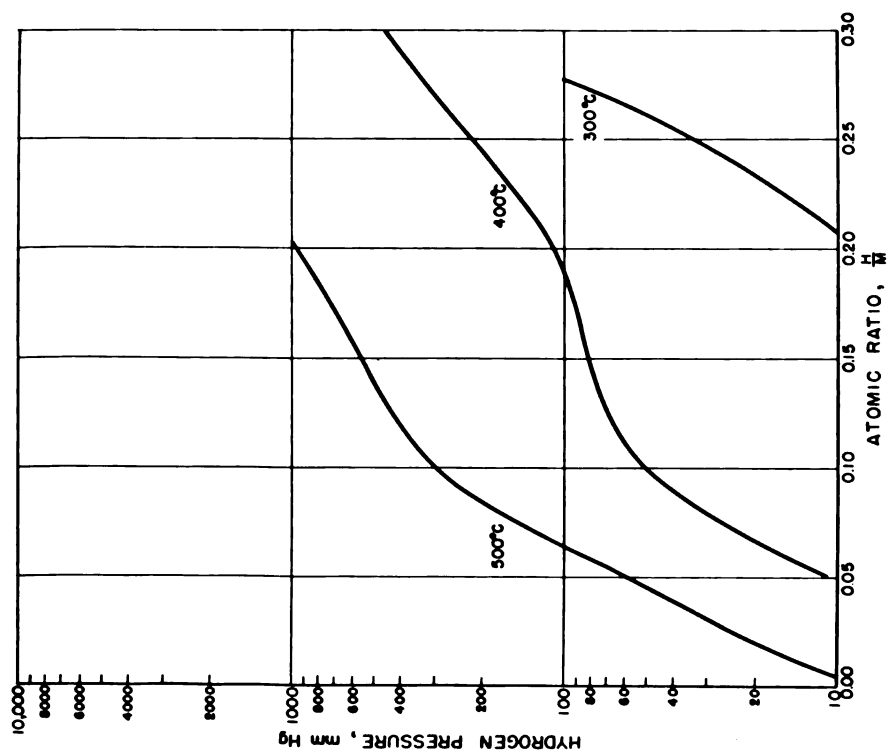


Fig. 1.10.2 — The Decomposition-pressure Isotherm for the System Niobium-Hydrogen. Submitted by Battelle Memorial Institute, May 1, 1952.

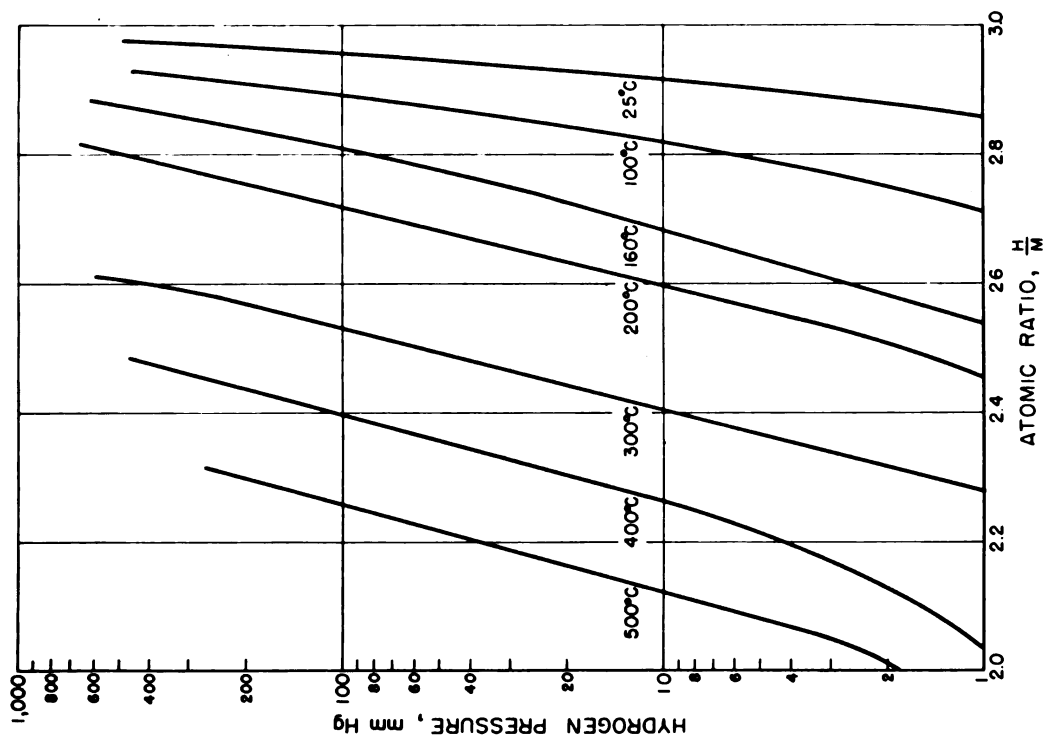


Fig. 1.10.4 — The Decomposition-pressure Isotherm for the System Plutonium-Hydrogen. Submitted by Battelle Memorial Institute, May 1, 1952.

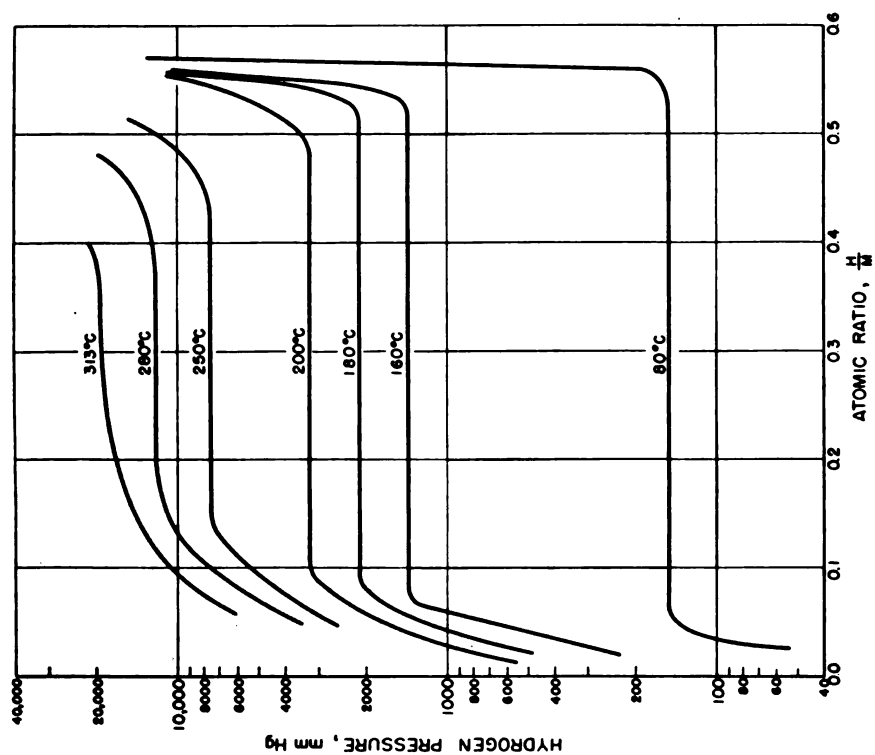


Fig. 1.10.3 — The Decomposition-pressure Isotherm for the System Palladium-Hydrogen. Submitted by Battelle Memorial Institute, May 1, 1952.

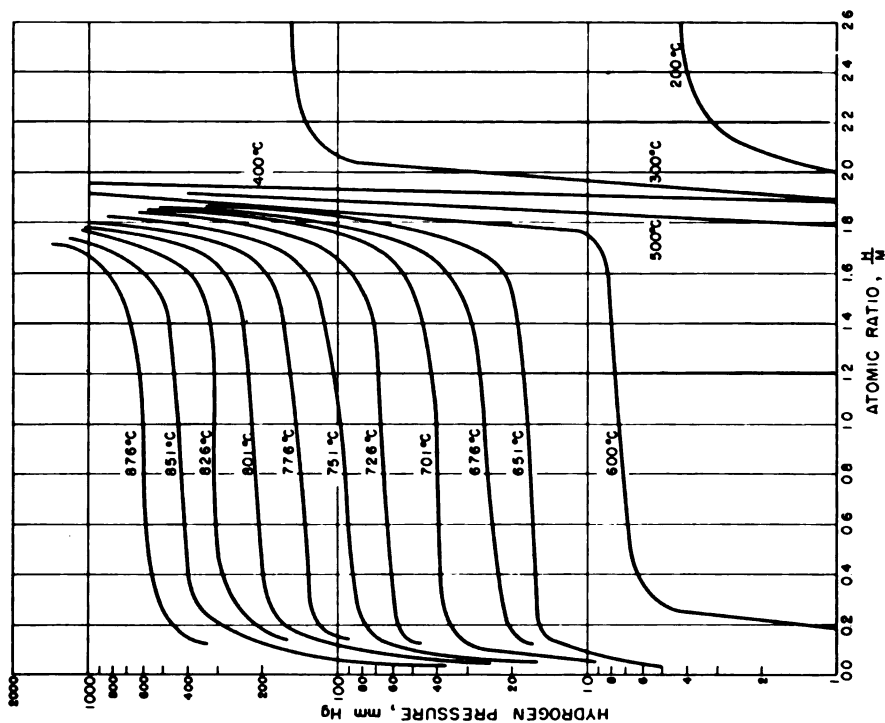


Fig. 1.10.6—The Decomposition-pressure Isotherm for the System Thorium-Hydrogen. Submitted by Battelle Memorial Institute, May 1, 1952.

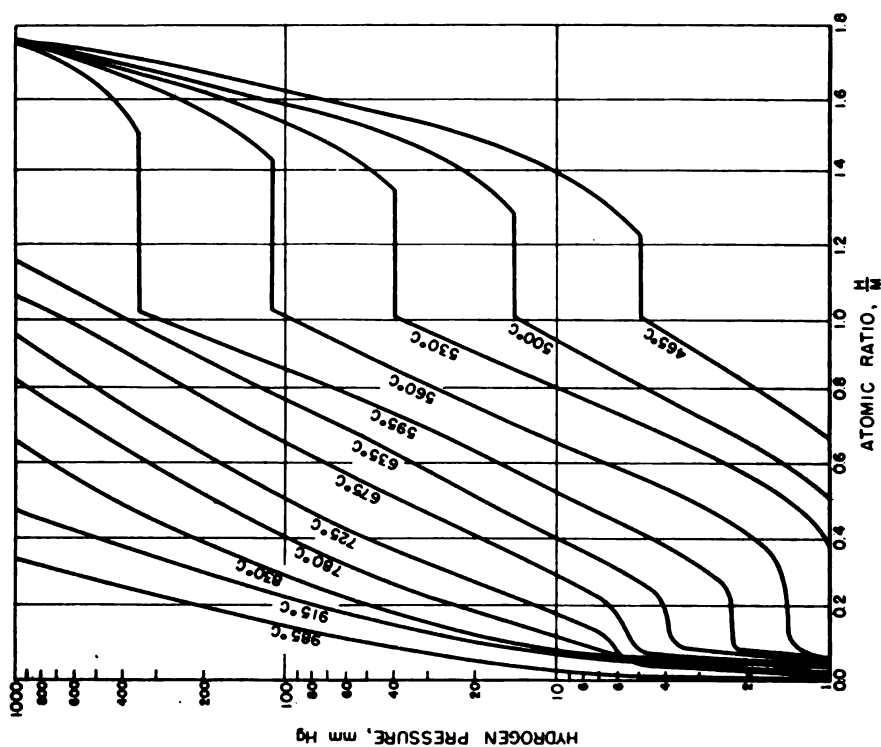


Fig. 1.10.5—The Decomposition-pressure Isotherm for the System Titanium-Hydrogen. Submitted by Battelle Memorial Institute, May 1, 1952.

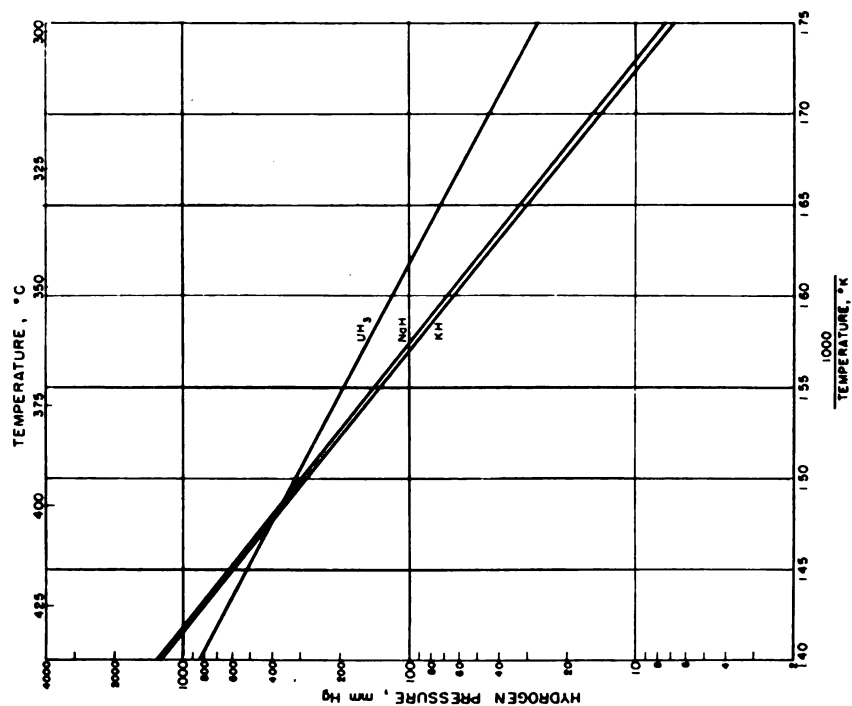


Fig. 1.10.8—The Hydrogen Pressure—Temperature Relations for the Compounds UH_3 , NaH , and KH . Submitted by Battelle Memorial Institute, May 1, 1962.

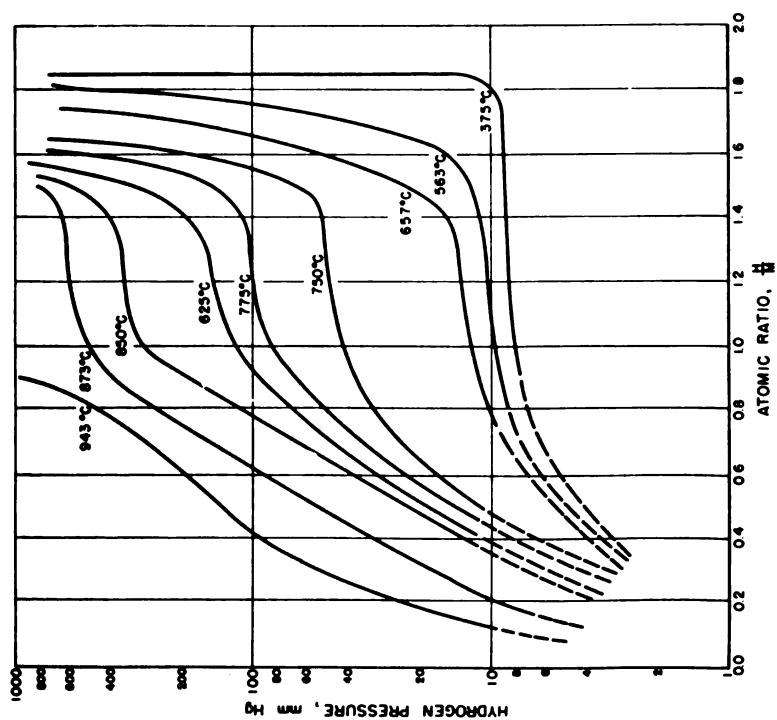


Fig. 1.10.7—The Decomposition-pressure Isotherm for the System Zirconium-Hydrogen. Submitted by Battelle Memorial Institute, May 1, 1962.

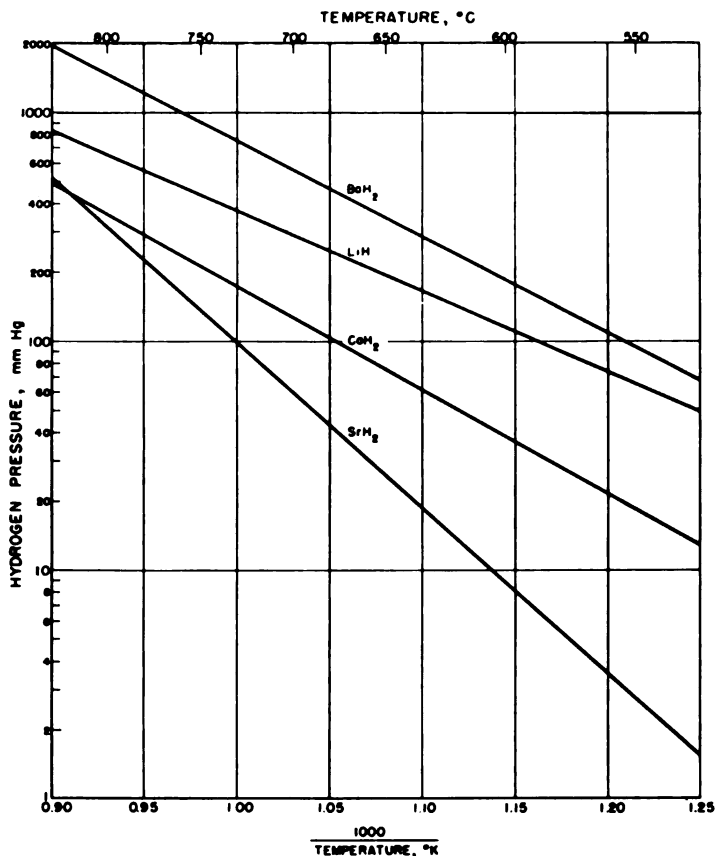


Fig. 1.10.9 — The Hydrogen Pressure–Temperature Relations for the Compounds BaH₂, LiH, CaH₂, and SrH₂. Submitted by Battelle Memorial Institute, May 1, 1952.

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CHAPTER 1.11

Lithium and Its Alloys

M. W. Mote and P. D. Frost

REACTOR APPLICATION

Isotopically separated lithium is of interest for use in a liquid-metal-cooled reactor.

ABUNDANCE AND AVAILABILITY

The most frequently reported figure for the concentration of lithium in the earth's crust is 4×10^{-3} percent, which is twice that of lead and six times the concentration of tin. Although lithium is widely distributed, occurring as the silicate, phosphate, chloride, and fluoride, very few economically exploitable deposits are known. It is believed that the United States possesses the largest and richest of these deposits. Other sources include Spain, South Africa, Germany, Czechoslovakia, and Canada.

The principal lithium-bearing minerals are spodumene, lepidolite, and zinnwaldite. These minerals occur in extensive deposits and are, therefore, useful sources of lithium even though the lithium content is not high.

The price of low-sodium lithium in 1950 was \$12.00/lb in 100-lb lots. Low-chloride, low-sodium lithium is available at a somewhat higher price. The principal sources in the United States are the Metalloy Corporation, Minneapolis, Minnesota, and the Maywood Chemical Company, Maywood, New Jersey.

EXTRACTION AND PURIFICATION

All methods of extracting lithium from its ores are based on three common steps: (1) formation of a water-soluble lithium salt, (2) purification of the solution, and (3) precipitation of the lithium as a carbonate. Chlorides and fluorides are water-soluble. Phosphate minerals are acid-soluble, and the acid chosen for production use is often HCl. After purification, the solution is evaporated to dryness with oxalic acid and the residue ignited to lithium carbonate.

The most important extraction method, however, was first proposed by Wadman and developed by von Giersewald and Weidman of Metallgesellschaft A. G. Silicate ores (spodumene or the lithium micas) are finely ground and mixed with potassium sulfate. The mixture is heated to some temperature below the melting point of the lowest melting constituent, variously reported as from 1320° to 1650°F. A complex and little-understood series of solid-state reactions take place, resulting in the formation of soluble Li_2SO_4 . An equivalent amount of potassium is found in the insoluble residue as a potassium mica.

The lithium sulfate is extracted with water and the solution purified, after concentrating, by precipitating iron, manganese, and other impurities with sodium hydroxide. The purified solution is evaporated still further to crystallize out the excess potassium sulfate. The decanted solution is then treated with potassium carbonate to precipitate lithium carbonate which is converted to LiCl for electrolytic recovery of the metal.

Lithium chloride is reduced in cells which are very similar to those used for magnesium. The bath is composed of equal amounts of potassium chloride and lithium chloride. The potassium chloride not only reduces the melting point and operating temperatures of the bath but also greatly increases the efficiency and permits continuous operation. Modern cells operate at a power efficiency of more than 90 percent and a metal recovery efficiency of more than 95 percent. The purity of the metal produced depends almost entirely upon the purity of the LiCl used in the cell. Present practice consistently produces 99.5 percent lithium or better.

PHYSICAL AND CHEMICAL CONSTANTS

Metallic lithium has been useful only as a constituent of an alloy, and hence, comparatively little effort has been made to determine the properties of the metal itself. The considerable variation in data reported on the properties of lithium reflects this lack of effort, but these discrepancies are probably attributable largely to variations in purity of the samples investigated. Evidence indicates that small amounts of impurities have a disproportionate effect on the properties of the sample, and lithium is so reactive that very pure metal is difficult to obtain.

Table 1.11.1 presents the best available information on the physical and chemical constants of lithium.

MECHANICAL PROPERTIES

Metallic lithium is soft and malleable. It is harder than sodium but is easily deformed by hammering at room temperature. Quantitative data are not available except that hardness is reported as 0.6 on Moh's scale.

MELTING AND CASTING

Pure lithium can be melted in an open iron or steel pot if it is protected by paraffin or light mineral oil. The melt can then be poured into molds that are open to the atmosphere. The use of a protective inert-gas atmosphere for melting and casting would eliminate the need for oil or paraffin. Both methods are used in melting and casting lithium alloys. For melting, steel and iron pots are recommended because oxide-base ceramic containers are readily attacked by molten lithium.

FORMING AND FABRICATION

Lithium can be forged, pressed, extruded, and rolled at room temperature. The metal does not work harden at room temperature which makes it unsuitable for drawing.

JOINING

No methods of joining lithium are reported. Welding by any of the ordinary methods would be extremely difficult because of the metal's low melting temperature and inherent

Table 1.11.1 — Physical and Chemical Constants of Lithium

Thermal-neutron-absorption cross section, barns/atom	67 ± 2
Density† (20°C), gm/cm ³	0.534
Melting point, °C	186
Boiling point, °C	1336 – 1372
Heat of fusion (186°C), cal/mole	1100
Heat of vaporization, cal/mole	36,100
Specific heat,‡ cal/(gm)(°C)	
– 200°C	0.542
– 100°C	.663
0°C	.784
50°C	.844
100°C	.905
186°C	1.010
Enthalpy (25°C), cal/gm	203 ± 0.7
Entropy (0°C), cal/(mole)(°C)	6.70 ± 0.06
Electrical resistivity (0°C), μohm-cm	8.55
Coefficient of linear thermal expansion (20°C), per °C	56 × 10 ⁻⁶
Thermal conductivity,§ cal/(sec)(cm)(°C)	
0°C	0.17
100°C	.17
Allotropic transformations, °C	
Body-centered cubic to face-centered cubic	– 196
Face-centered cubic to body-centered cubic	– 117
Crystallography, A	
α (BCC) 20°C	a ₀ = 3.502
β (FCC) – 196°C	a ₀ = 4.41
Health hazards	None known
Handling and storage	Less reactive in air or water than sodium, potassium, rubidium, or cesium. Can be handled in air and stored in dry kerosene or light mineral oil. Some authorities consider that a violent reaction with halogenated hydrocarbons is likely; therefore, only clean, pure kerosene or oil should be used. Lithium fires are best controlled by G-1 powder. Standard extinguishers, even the CO ₂ type, are ineffective and their use can be dangerous.

$$\dagger \text{Gm/cm}^3 \times 62.43 = \text{lb/cu ft}$$

$$\ddagger \text{Cal/(gm)(}^\circ\text{C)} \times 1 = \text{Btu/(lb)(}^\circ\text{F)}$$

$$\S \text{Cal/(sec)(cm)(}^\circ\text{C)} \times (2.419 \times 10^3) = \text{Btu/(hr)(ft)(}^\circ\text{F)}$$

tendency to react with the air when molten. Lithium could conceivably be arc-welded in an inert atmosphere using the lowest possible power input. It is also possible that lithium could be resistance-welded.

Protecting the surface from oxidation would be the principal problem associated with soldering. The metal surface tarnishes very rapidly in air.

MACHINING

Because of its extreme softness and high reactivity, lithium is not amenable to machining operations. The chips tend to ignite when heated much above room temperature. Slow speeds and proper coolants might combat this problem, but the softness of the metal would still make machining of any kind extremely difficult.

CORROSION BEHAVIOR

Lithium of commercial purity tarnishes in moist air in a matter of seconds and even quite rapidly in dry air. The rate of attack decreases as the thickness of the oxide-nitride film increases. At room temperature, lithium is more reactive than magnesium but much less so than the other alkali metals. The formation of the nitride (Li_3N) is catalyzed by moisture in the air, and it forms more readily than the oxide. Lithium reacts with water to release hydrogen. The reaction is not as violent as that between sodium and water, and the heat released is not sufficient to melt the lithium.

Lithium reacts at red heat directly with hydrogen, forming the relatively stable LiH . This hydride can be fused, electrolyzed, and handled similarly to salts of the halogen family.

Halides are formed readily at elevated temperatures by direct reaction of the halogens with lithium. Lithium chloride is more deliquescent than calcium chloride and tends to form the crystalline hydrate.

A reaction between lithium and carbon dioxide produces lithium oxide or lithium carbonate and carbon. This reaction precludes the use of CO_2 extinguishers for lithium fires. Lithium also reacts with ammonia gas, forming the amide.

The most satisfactory container materials for molten lithium are the ferrous metals, niobium, molybdenum, and tantalum.

PROTECTIVE TECHNIQUES

No method of plating, painting, or cladding to protect lithium is known.

PHASE DIAGRAMS

Phase diagrams of lithium with other metals have been collected in the Report on Lithium, D. S. Jesseman, W. K. Anderson, and V. P. Calkins, NEPA 1193, October 20, 1949.

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CHAPTER 1.12

Magnesium and Its Alloys

M. W. Mote and P. D. Frost

At the present time, no large-scale reactor application of magnesium exists. However, the low thermal-neutron-absorption cross section and high strength-to-weight ratio of magnesium make it a material of potential utility.

Magnesium has a specific gravity of only 1.74, which makes it the world's lightest structural metal. Compared with magnesium, aluminum is $1\frac{1}{2}$ times heavier, steel and iron are 4 times heavier, and nickel and copper alloys are 5 times heavier. Aside from its light weight, magnesium has several characteristics which make it an important structural alloy. It has excellent machinability and may be cast and fabricated by practically every method employed in the metal industry. The fact that it is amenable to heat treatment further enhances its properties.

Like the majority of structural metals, magnesium is not used in the pure state for stressed applications but is alloyed with other metals such as aluminum, zinc, zirconium, and manganese to obtain the necessary strength for structural applications. Table 1.12.1 lists the nominal composition of selected magnesium alloys.

Table 1.12.1—Nominal Composition of Selected Magnesium Alloys

Alloy designation	Alloy composition, %					Mg
	Al	Zn	Mn	Zr	Rare earths	
Dowmetal C	9.0	2.0	0.2	Balance
Dowmetal H	6.0	3.0	0.2	Balance
Dowmetal R	9.0	0.6	0.2	Balance
Dowmetal FS and FS1	3.1	1.0	Balance
Dowmetal M	1.2	Balance
Dowmetal J1	6.5	1.0	Balance
Dowmetal O1	8.5	0.5	Balance
Dowmetal ZK60A	...	5.7	...	0.55	...	Balance
Dowmetal ZK61	...	6.7	...	Balance
EK 3034	3.23	Balance
EK 3159	3.21	Balance
EK 6037	6.21	Balance
EZ 33	...	3.0554	2.42	Balance
ZRE1	...	2.5–3.06	2.5	Balance
E 3	3.23	Balance
AZ9Z	9.5	2.0	Balance

ABUNDANCE AND AVAILABILITY

Magnesium is the third most plentiful commercial metal in the earth's crust. Its ores are not only plentiful but are readily adaptable to modern methods of beneficiation and extraction. The principal ores are dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$), magnesite (MgCO_3), and carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$). Magnesium also occurs as magnesium chloride in certain natural salt brines. These brines were the principal source of magnesium produced in this country prior to World War II. Another and essentially inexhaustible source of magnesium is sea water, which contains approximately 0.5 percent magnesium chloride. Although 0.5 percent magnesium chloride would seem to be a very dilute source of magnesium, the means of extraction and separation are highly developed and economical, and the yield of a cubic mile of sea water is about 9 billion pounds of metallic magnesium.

Prior to World War I, the lack of alloys suitable for structural purposes discouraged the production of magnesium and kept the price high, in the range of \$5.00/lb. Increased production during World War I resulted in a reduction of the price of magnesium to approximately \$2.00/lb. The market price of commercially pure magnesium in July, 1952, was approximately \$0.27/lb.

EXTRACTION AND PURIFICATION

Military demands for magnesium have led to the simultaneous development of several successful methods for the production of primary magnesium. The three processes used principally in the United States are: electrolytic, thermal reduction by carbon, and thermal reduction by silicon. The portion of primary magnesium produced by each of these processes is 72 percent, 4 percent, and 24 percent, respectively.

The electrolytic method utilized anhydrous magnesium chloride as the cell feed. Practice does vary, however, in the choice of raw materials and the methods employed to produce anhydrous magnesium chloride. The Dow Chemical Company, for example, obtains its magnesium chloride by the following process: Sea water containing approximately 0.13 percent magnesium is pumped into large settling tanks and mixed with lime obtained, as a rule, by roasting oyster shells dredged from the ocean floor. The calcium of the lime replaces magnesium in the sea water, and the insoluble magnesium hydroxide is precipitated. The magnesium hydroxide is removed from the bottom of the settling tanks and filtered. The precipitate is then treated with hydrochloric acid, which is prepared from natural gas and chlorine, and the resulting magnesium chloride is passed through evaporators and dryers. The dry powder is the cell feed for the electrolytic process. The electrolysis of molten anhydrous magnesium chloride results in primary magnesium metal and chlorine gas, which is returned to the process for the production of the hydrochloric acid.

Thermal-reduction processes justify their existence by being independent of direct-current electricity as a source of power and because they can be built and put into operation quickly. The carbothermic process consists of mixing magnesium oxide and a suitable form of carbon in a closed electric-arc furnace and heating to a temperature somewhat above 3600°F. Magnesium is liberated as a vapor and is then solidified by shock cooling at lower temperatures. The condensate is a fine dust which must be formed into briquettes and then distilled to produce ingot metal. This method is known as the Hansgird process.

The second reduction process, commonly called the Pidgeon process, comprises the reduction of calcined magnesite or dolomite by ferrosilicon. The two reduction constituents are briquetted in the correct proportions and placed in cylindrical retorts which have been

highly evacuated. The reduction temperature is about 2100°F. After reduction, the magnesium vapor condenses in the cooler end of the retort in the form of crystalline rings of metal.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants of magnesium are given in Table 1.12.2, while Table 1.12.3 lists selected constants for some magnesium alloys.

CRYSTALLOGRAPHY

The crystal structure of pure magnesium is close-packed hexagonal, with $a_0 = 3.203\text{Å}$, $c_0 = 5.199$ and $c/a = 1.624$. The primary slip plane (0001) is operative between 20° and 225°C, and the secondary slip plane (10 $\bar{1}$ 1) is operative above 225°C. The twinning plane is (10 $\bar{1}$ 2). The cleavage plane is (0001). The minimum interatomic distance is 3.190Å.

MECHANICAL PROPERTIES

The modulus of elasticity of pure magnesium is 6.5×10^6 lb/sq in. The modulus of rigidity is 2.42×10^6 lb/sq in., and Poisson's ratio is 0.35.

ALLOYS FOR LOW-TEMPERATURE APPLICATIONS

Table 1.12.4 gives some mechanical properties of commercial magnesium alloys used most extensively for room-temperature applications.

Some magnesium-lithium alloys not commercially available possess interesting fabrication properties. The chief advantages which lithium confers on magnesium are decreased density and increased ductility. Table 1.12.5 compares the tensile properties of several magnesium-lithium alloys with those of pure magnesium.

The increased ductility of the magnesium-lithium alloys is most striking in fabrication. Lithium markedly improves the bend ductility of magnesium as extruded, hot rolled, or cold rolled. Furthermore, the lithium-bearing alloys can be cold rolled to large reductions without cracking, whereas pure magnesium cannot be. High-strength, magnesium-lithium alloys are easily forged directly from the cast condition; magnesium-base alloys must first be extruded to break up the cast structure, then forged.

The high-strength, magnesium-lithium-base alloys may contain zinc, aluminum, cadmium, or silver. The best combinations of strength and ductility are obtained when enough lithium is present to make the alloys entirely body-centered cubic. This requires about 11 percent lithium. Mechanical properties of some of the high-strength alloys are shown in Table 1.12.6.

The low density of the high-strength alloys combined with their high strength makes them attractive for certain structural applications. There is, however, a serious obstacle which has prevented the alloys from being used commercially; namely, they lose strength by over-aging at temperatures of 150° to 200°F.

This problem is associated with the lithium alloys, since the b.c.c. lattice is strengthened by a precipitation-hardening mechanism involving the phase MgLi_2X , where X may be aluminum, zinc, cadmium, or silver. By decreasing the quantity of lithium so that the alloys contain both the b.c.c. and the h.c.p. phases, the strength is improved. Unfortunately, the low-lithium alloys have less ductility and higher densities than the high-lithium alloys. Although they can be forged and extruded at elevated temperatures more readily than commercial magnesium alloys, they must be warm formed and can tolerate little cold rolling.

Table 1.12.2—Physical and Chemical Constants of Magnesium

Thermal-neutron-absorption cross section, barns/atom	0.059 ± 0.0042
Density, gm/cm ³ *	
20°C	1.74
650°C (solid)	1.64
650°C (liquid)	1.57
700°C	1.54
Melting point, °C	650
Boiling point, °C	1120
Heat of fusion, cal/gm	88.8
Heat of vaporization, cal/gm	1300
Heat of combustion, cal/mole	145,000
Specific heat (25°C), cal/(gm)(°C)†	0.25
Coefficient of linear thermal expansion, per °C	
20°–100°C	25.8 × 10 ⁻⁶
20°–300°C	27.0 × 10 ⁻⁶
20°–500°C	29.9 × 10 ⁻⁶
Thermal conductivity (20°C), cal/(sec)(cm)(°C)‡	0.376
Electrical resistivity, μohm-cm	
20°C	4.46
300°C	10
650°C (solid)	15
650°C (liquid)	35
1000°C	39
Entropy (S _T – S _{0°C}), cal/(mole)(°C)	
123°C	1.77
423°C	5.48
650°C (solid)	7.48
650°C (liquid)	9.82
823°C	11.12
Enthalpy (H _T – H _{0°C}), cal/mole	
123°C	615
423°C	2615
650°C (solid)	4230
650°C (liquid)	6390
823°C	7700

*Gm/cm³ × 62.43 = lb/cu ft

†Cal/(gm)(°C) × 1 = Btu/(lb)(°F)

‡Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

Table 1.12.3—Selected Physical Constants of Magnesium and Some Magnesium Alloys

Constant	Alloy, Dowmetal designation						
	Pure Mg	C	H	FS and F81	M	J1	ZK60A
Density (20°C), gm/cm ³ *	1.74	1.82	1.83	1.77	1.76	1.80	1.83
Melting point, °C	650	599	612	627	649	618	635
Electrical resistivity (20°C), μohm-cm	4.46	16	11.5	10.0	5.0	12.5	...
Thermal conductivity (20°C), cal/(sec)(cm)(°C)†	0.376	0.16	0.18	0.23	0.30	0.19	...
Coefficient of linear thermal expansion (20°–100°C), per °C	26 × 10 ⁻⁶	26 × 10 ⁻⁶	26 × 10 ⁻⁶	26 × 10 ⁻⁶	26 × 10 ⁻⁶	26 × 10 ⁻⁶	...
Specific heat (25°C), cal/(gm)(°C)‡	0.25	0.25	0.25	0.25	0.25	0.25	0.25

*Gm/cm³ × 62.43 = lb/cu ft†Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

‡Cal/(gm)(°C) × 1 = Btu/(lb)(°F)

**Table 1.12.4—Mechanical Properties of Commercial Magnesium Alloys
for Room-temperature Applications**

Alloy designation*	Available form	Alloy condition†	Yield strength,	Ultimate strength,	Elongation,	Compressive yield strength,	Shear strength,	Bearing strength,		Hardness	
			10 ³ lb/sq in.	10 ³ lb/sq in.	in 2 in., %	10 ³ lb/sq in.	10 ³ lb/sq in.	10 ³ lb/sq in.	Ultimate Yield	Brinell	Rockwell "E"
C	‡	F	14	24	2	14	19	60	48	65	77
		T-2	14	24	2	...	19	60	48
		T-4	14	40	10	14	20	75	48	63	75
		T-6	23	40	2	23	21	85	65	84	90
H	‡	F	14	29	6	14	18	65	42	50	59
		T-2	14	29	5	...	19	65	42
		T-4	14	40	12	14	19	70	42	55	66
		T-6	19	40	5	19	21	80	56	73	83
R	‡	F	14	24	2	52	62
		T-4	14	40	11	53	64
		T-6	19	40	4	66	77
(RC)	§	F	22	33	3	22	20	60	72
FS and FS1	¶	O	22	37	21	16	21	75	36	56	67
		H-24	32	42	16	27	23	78	53	73	83
	**	F	22	37	21	...	21	75	36
		F	26	37	12	15	19	65	35	49	57
		††	23	35	12	15	46	61
M	¶	O	18	33	16	12	18	60	28	48	55
		H-24	28	37	7	20	17	56	67
		F	...	33
	**	F	20	34	9	12	18	56	28	44	45
		††	20	32	8	10	42	41
J1	**	F	30	44	14	19	19	74	43	60	72
		††	24	41	13	16	50	60
O1	**	F	32	48	12	...	22	76	50	60	77
		T-5	36	52	5	33	24	90	62	82	88
ZK60A	**	F	38	49	12	33	24	73	51	75	84
		T-5	42	51	10	34	25	76	55	82	88
	††	F	34	46	11	24	75	84
		T-5	44	52	9	30	82	88
ZK61 (ASTM)	‡‡	T-5A	26	42	8
		T-6	30	47	10

*For compositions see Table 1.12.1

†Alloy conditions

F—as fabricated

H-24—hard rolled

O—annealed

T-2—cast and stabilized

T-4—solution heat treated

T-5—aged

T-5A—aged at room temperature

T-6—solution heat treated and aged

‡Sand and permanent mold castings

§Die castings

¶Sheet

**Extruded solid shapes

††Extruded hollow shapes

‡‡Sand castings

Table 1.12.5—The Tensile Properties of Magnesium and Some Magnesium-Lithium Alloys

Nominal wt-% lithium	Yield strength, lb/sq in.	Ultimate strength, lb/sq in.	Elongation in 1 in., %	Density, gm/cm ³
Commercially pure Mg	14,000	27,000	16*	1.74
3	12,500	20,200	23	1.86
9.1	13,900	18,300	36	1.51
16.7	10,300	14,500	34	1.33

*In. 2 in.

Table 1.12.6—Mechanical Properties of Some Extruded High-strength Magnesium-lithium-base Alloys*

Intended composition, wt-%					Lattice structure	Tensile yield strength, lb/sq in.	Ultimate tensile strength, lb/sq in.	Elong. in 2 in. %	Hardness, Rockwell "E" scale	Compressive yield strength, lb/sq in.
Li	Al	Zn	Cd	Ag						
10.5	...	4	6	6	b.c.c.	46,000	51,500	8	90.5	54,800
10.9	...	3	7	3	b.c.c.	38,500	41,600	22	90	42,900
12.0	...	4	6	6	b.c.c.	52,200	53,400	1	84.5	54,200
3.92	2	h.c.p.	23,000	34,000	16
3.84	4	h.c.p.	26,000	39,000	15
3.76	6	h.c.p.	28,000	44,000	11
3.68	8	h.c.p.	32,000	42,000	4
10.9	0.5	b.c.c.	22,000	24,000	39
10.8	2	b.c.c. + h.c.p.	28,000	32,000	23
10.3	6	b.c.c. + h.c.p.	30,000	37,000	20
9.7	12	b.c.c. + h.c.p.	33,000	44,000	3

*The elastic modulus of magnesium-lithium alloys is 6.5×10^6 lb/sq in.

ELEVATED-TEMPERATURE APPLICATIONS*

The low neutron-capture cross section of magnesium makes it an interesting material for reactor application. However, the retention of a low neutron-capture cross section in alloys restricts the number of elements with which magnesium may be alloyed for strengthening purposes. The alloying elements which would least increase the capture cross section of magnesium are aluminum, calcium, lead, silicon, tin, and zirconium. Additions of beryllium and bismuth would reduce the cross section. However, beryllium, bismuth, lead,

*For a complete description of the properties of magnesium alloys at room and elevated temperatures, refer to Technical Survey Report on The Effects of Temperature on the Mechanical Properties of Magnesium Alloys to Project RAND, Craighead, C. M., et al., R-146, Battelle Memorial Institute, April 29, 1949.

silicon, and tin are not good alloying components because they are not particularly effective in strengthening magnesium, especially at elevated temperatures.

Magnesium alloys containing up to 0.5 to 1.0 percent pure cerium offer the most promise for elevated-temperature applications where neutron-capture cross section is an important limiting factor. Alloys containing aluminum and zirconium exhibit exceptionally high strengths at room temperature, but their elevated-temperature properties, particularly creep resistance, are low. The alloys with magnesium, aluminum, and zirconium must be prepared by the powder-extrusion method because of the incompatibility of aluminum and zirconium in molten magnesium which results in a precipitation of the zirconium from the alloy.

Table 1.12.7—Creep Limits for Several Magnesium Alloys

Alloy*	Force to effect 0.5% total extension, lb/sq in.				
	200°F	300°F	400°F	500°F	600°F
KO	2,100	1,600
KO + 6%A33	3,500	2,400
KO + 12%A33	4,000	2,300
Mg + 1%Th	8,600	6,200	2,000
Mg + 2%Th	9,600	7,100	2,000
Mg + 3%Th	10,000	7,200	2,100
Mg + 0.85% pure Ce	9,300	4,200	1,200
Mg + 2.23% pure Ce	9,600	3,300	1,100
Mg + 4.39% pure Ce	9,300	2,900	1,100

*Alloy KO consists of Mg + 0.5% Zr; Alloy A33 consists of Mg + 33% Al

Magnesium-zirconium-calcium alloys are definitely superior to magnesium-zirconium-aluminum alloys, both in strength and creep resistance at moderately elevated temperatures. These alloys cannot, however, compete with magnesium-cerium alloys in creep resistance. Two percent thorium, 1 percent cerium, and 7 percent aluminum are equally effective in increasing the neutron-capture cross section of magnesium. The same comparison may be made for 1 percent thorium, 0.5 percent cerium, and 4 percent aluminum.

The creep limits for several alloys in the range 200° to 600°F, expressed as the force necessary to effect a 0.5 percent total extension in the creep specimen in 100 hr, are given in Table 1.12.7.

Tables 1.12.8 and 1.12.9 present tensile and creep data for magnesium casting alloys in the temperature range 70° to 600°F.

MELTING AND CASTING*

MAGNESIUM FOR CASTING

The major application for magnesium alloys is in sand castings, covering a wide variation in complexity of design. Production castings are being made varying in size from a few ounces to as much as 1000 lb.

* Material excerpted from Metals Handbook (1948), published by The American Society for Metals, pp 969-974.

Table 1.12.8—Tensile Properties of Some Magnesium Alloys at Elevated Temperatures

Alloy designation*	Alloy condition†	300°F				400°F				500°F				600°F			
		Yield strength, 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Elongation, 2 in., %	Yield strength, 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Elongation, 2 in., %	Yield strength, 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Elongation, 2 in., %	Yield strength, 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Elongation, 2 in., %	Yield strength, 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Elongation, 2 in., %	
EK-30	T-6	16.5	22.9	2.4	14.7	20.8	7.7	14.0	20.0	13.1	12.1	17.5	29.7	7.7	11.8	69.6	
EK-31	T-6	19.8	26.5	2.9	17.0	22.0	11.2	16.5	21.4	13.0	13.4	18.6	21.5	9.2	13.3	52.0	
EK-60	T-6	19.7	23.7	0.5	18.0	21.0	1.0	17.0	21.0	2.0	14.0	19.2	4.8	9.0	14.1	38.0	
T-5	EZ-33	13.4	17.4	1.8	10.0	22.0	11.8	9.0	20.0	19.0	9.0	17.0	35.0	
EZ-33	T-6	13.3	19.6	1.5	11.3	21.3	15.0	10.7	18.7	16.2	9.6	13.7	44.2	6.2	8.9	64.0	
ZR-E1	T-5A	12.3	20.3	3-6	10.5	20.1	20-25	
E-3	T-6	26.0	41.9	2.0	18.0	34.2	37.0	10.9	16.9	36.0	8.5	12.6	52.0	4.7	7.6	108	
A292	T-6	12.4	20.5	1.5	12.9	17.9	7.0	11.9	16.8	4.7	11.3	17.9	11.7	8.8	13.5	24.2	

* See Table 1.12.1 for compositions

† T-5 = aged; T-5A = aged at room temperature; T-6 = solution heat treated and aged

Table 1.12.9—Creep Properties of Some Magnesium Alloys

Alloy designation*	Alloy condition†	400°F				500°F				600°F			
		0.1% Creep extension		0.5% Total extension		0.1% Creep extension		0.5% Total extension		0.1% Creep extension		0.5% Total extension	
		Creep Limit in 100 hr, 10 ³ lb./sq in.											
EK-30	T-8	7.9	7.2	10.1	2.5	2.5	3.6	4.4	1.3	1.3	1.5	1.7	
EK-31	T-8	8.8	8.0	11.2	3.4	3.6	4.4	4.4	1.3	1.3	1.5	1.7	
EK-60	T-6	8.8	8.0	11.0	3.0	3.3	4.2	4.2	1.1	1.1	1.3	1.7	
EZ-33	T-5	8.4	8.0	9.8	3.7	3.9	5.0	5.0	1.2	1.2	1.4	1.8	
EZ-33	T-6	8.0	7.7	9.5	3.0	3.5	4.7	4.7	1.1	1.1	1.4	1.9	
ZR-E1	T-9A	9.4	7.8	10.0	
E-3	T-6	10.0	8.4	10.2	4.7	4.7	6.2	6.2	2.3	2.3	2.5	2.8	
A292	T-6	3.3	3.5	6.2	0.9	0.9	1.3	...	0.4	0.4	0.6	1.1	

* See Table 1.12.1 for compositions

† T-5 = aged; T-5A = aged at room temperature; T-6 = solution heat treated and aged

Crucibles fabricated from steel plate are used for melting and casting magnesium alloys and vary in capacity from approximately 60 to 1000 lb. These crucibles are heated with either gas or oil, and under normal conditions of operation, the products of combustion have no effect on the quality of the metal.

Since boiler plate, when unprotected, scales badly under conditions of use, it has been found desirable, both for safety and for economy, to protect the crucibles by treatment with aluminum. This is accomplished by spraying aluminum on the sandblasted or grit-blasted steel surface and then heat treating to alloy the aluminum with the steel.

During melting, a cover of flux is used to prevent oxidation or burning. The fluxes used in melting magnesium alloys are mixtures of chlorides with small amounts of other materials. Since magnesium chloride is a major constituent, the fluxes are hygroscopic.

After the casting crucible has been filled, either from the premelt furnace or by melting directly in the crucible, the metal must be stirred thoroughly to clean it. This can be done by means of an iron stirring rod or by treatment with chlorine gas.

The use of chlorine gas in magnesium foundry melting practice has been developed recently and is similar to that used in aluminum melting. It not only removes gas from the metal, thus decreasing trouble from microporosity, but also stirs and cleans the metal, replacing hand stirring. The gas is bubbled through the melt in the casting crucibles at about 1350°F for the length of time necessary to remove the dissolved gas, usually between 5 and 15 min. The gas is bubbled through the metal at the highest rate possible without spattering metal from the crucible.

The grain size of the cast metal is refined by superheating, and the mechanical properties are improved. Superheating practice varies somewhat in different foundries. In general, 5 to 15 min at a temperature of 1650°F, or heating to 1700°F, gives good grain refining. For best results, the crucible should be removed from the furnace at a temperature of about 1650°F and should be cooled in air to the casting temperature.

MAGNESIUM FOR WORKING

Furnaces for melting, alloying, refining, settling, and casting magnesium alloys are generally of the pot type, heated by gas or oil, and have capacities of 100 to 4000 lb. Pots are usually made of cast or welded steel protected with a sprayed-metal coating for longer service. Though all operations may be performed in the same furnace, a product of higher quality can be obtained when separate pots are used for settling and casting.

Prealloyed pig may be used for preparing all wrought magnesium; however, in large-scale operations it may be advantageous to use magnesium pig and perform the alloying operation.

High-purity aluminum and zinc are added immediately after the melting by placing small pieces in the alloying tool and immersing it just below the surface of the melt. Beryllium is added in the same manner and at the highest possible temperature. About 50 percent of the beryllium is recovered when the proper amount of a 5 percent beryllium-aluminum master alloy is added to obtain a 0.0005 percent beryllium content in the melt. Calcium is introduced into the melt 15 to 30 min before casting is started to avoid excessive losses. It may be introduced as a master alloy of 20 percent calcium in magnesium or in the pure form. Good uniformity of calcium throughout an entire cast is difficult to obtain; however, with close control, maximum variations of 0.015 percent and recoveries of 75 percent are obtainable. Recovery will be decreased by increase in temperature, holding time, and amount of flux present.

Refining is performed by the introduction of a manganese flux to condition the melt for the removal of iron in settling, and to agglomerate oxides and other impurities. When the temperature of the melt is between 1360° and 1400°F, a manganese flux is sprinkled on the bath and stirred simultaneously. The addition is made in order to produce in the melt, before settling, the desired percentage of manganese and is based on an 80-percent re-

covery of the manganese contained in the flux. After refining, settling is performed to precipitate iron, the agglomerated oxides, and other impurities.

During the melting, refining, and settling processes, oxides and impurities settle to the bottom of the pot and intermingle with excess flux to form a "heel" of sludge. In transferring or casting, care is taken not to disturb this heel of sludge; after the transferring operation, the heel is removed. Prior to sludging, the walls of the pot are scraped clean to prevent a build-up of magnesium oxide, which would reduce melting efficiency.

FORMING AND FABRICATION

EXTRUSION

Several magnesium extrusion alloys are commercially available. The alloys containing aluminum and zinc have higher strength, and their strength increases with aluminum content. Both direct and indirect extrusion presses have been used for the extrusion of magnesium alloys. Such presses vary from 250 to 5,500 tons. The billets to be used for extrusion are cast either by the direct-chill process or in permanent molds and are usually preheated in an electric- or gas-heated furnace prior to extrusion.

The pressures used for extruding magnesium vary from 50,000 to 100,000 lb/sq in. depending upon the composition of the alloy, the extrusion temperature, extrusion speed, length of billet, diameter of container, amount of reduction, and complexity of the cross section. The properties of a given alloy in the extruded form will vary with the speed of the extrusion. This is caused by the increase in temperature of the metal in the region of the die. Extrusions are available in a wide variety of section shapes and sizes in lengths up to about 30 ft.

ROLLING

Rolling is used chiefly for the fabrication of sheet and plate, most of which is produced from extruded slabs. A round ingot, 14 or 16 in. in diameter, is extruded into slabs 3 by 9 in. or 4 by 12 in. During extrusion, the cast structure is broken up under compression loading, whereas in rolling or forging, tensile loading as well as compression loading is involved.

Magnesium is inherently more subject to cracking under tensile loads than aluminum-, copper-, or iron-base alloys. It is expedient, therefore, to extrude the cast ingots prior to forging or rolling operations when this is possible.

The two factors that dictate magnesium rolling practices are: (1) a much greater amount of deformation is possible in hot working than in cold working; and (2) the maximum hot-rolling temperature is relatively low and the safe working range is narrow.

Magnesium plate ($\frac{1}{4}$ -in. gauge and heavier) is hot rolled to gauge. Practices for the fabrication of magnesium sheet (lighter than $\frac{1}{4}$ -in. gauge) have been developed to use maximum amounts of hot rolling to take advantage of the economies of larger reductions. Temperatures employed for hot rolling vary between 575° and 850°F, depending on the alloy and the gauge at which the reheating occurs. Reductions per pass vary greatly, depending upon the alloy and the hot-rolling conditions.

Cold rolling is usually used in the final stages of the production of sheet in order to control flatness and to improve mechanical properties. Annealing operations are necessary between successive stages of cold rolling. They may also be used after hot rolling, although they are not always necessary. Annealing temperatures vary from 600° to 800°F.

Magnesium rolled plate and sheet are available in thicknesses from about 0.016 in. to 1 in., and in widths and lengths up to 48 in. and 144 in., respectively. Strip is furnished in widths up to 8 in. Coiled strip is available in lengths up to 125 ft.

FORGING

The forging of magnesium alloys presents a problem not commonly encountered in structural metals. All magnesium alloys tend to move laterally instead of longitudinally when forged. "Drawing out," "fullering," and "rolling" operations must be performed, therefore, under carefully controlled conditions. These require that the dies for such operations be specifically designed for each job, and that the contour of the dies be carefully proportioned in such a manner that the metal is forced to move longitudinally.

Most magnesium forgings are made from extruded billets. In general, it is best to forge the magnesium alloys in hydraulic or slow-stroke mechanical presses. Some of the newer rapid-stroke vertical and horizontal presses are not suitable for forging magnesium alloys. These presses, like hammers, cause shearing and cracking of the metal during forging if considerable movement is involved, because the metal flows too rapidly.

Temperatures used for forging magnesium alloys vary from about 650° to 850°F. The temperature used is determined by the composition of the alloy, section size of the forging, and method of forging. For most alloys and forgings, temperature control to $\pm 25^\circ\text{F}$ is imperative. At lower temperatures, the dies may be difficult to fill and the metal may crack. Higher temperatures may result in dimensional imperfections or impaired physical properties. When forgings are made in several operations, it is considered good practice to lower the temperature with each pass to avoid excessive grain growth. Die temperatures must be maintained relatively high, in order to avoid chilling the stock as it flows.

Dies for forging magnesium alloys should be designed according to the practice employed for dies used with aluminum, except that corner radii and fillets should be made as generous as possible. Large radii and fillets promote better filling of a die.

The best lubricants currently available for use in forging contain graphite either in flake or colloidal form. The graphite is suspended in mineral or animal oil or occasionally in water. This graphite is difficult to remove from finished forgings except by mechanical means, such as sandblasting. The development of an improved lubricant that contains no graphite but that has adequate lubricating qualities is greatly desired by the magnesium forging industry. Wherever possible, the use of die lubricants that contain no graphite is recommended for superior forging surfaces.

OTHER METHODS OF FABRICATION

Magnesium sheet and extrusions are formed into useful shapes in much the same manner as other common metals, and the same type of fabricating equipment is used. Most operations are performed hot, particularly those requiring deep draws and small-radius bends. Both the tools and the work material are heated. As a consequence, deformation is easy with little or no spring-back.

Fabrication methods most frequently applied to magnesium alloys include press drawing, forming in rubber, forming under a drop hammer, hand forming, stretch forming, bending, and spinning. Certain variations between forming practices employed on other alloys and those practices employed on magnesium alloys are dictated by the high-temperature requirements. Several factors determine the temperature to which a sheet must be heated for forming. The composition and temper of the sheet are the most important of these factors. Hard-rolled sheet is used for parts in which a moderate amount of shaping is required. In order to maintain desired mechanical properties, forming temperatures between 325° and 500°F are used for hard-rolled sheet. Temperatures as high as 650°F are used for full-annealed sheet.

POWDER-METALLURGY TECHNIQUES

Conventional methods of preparing powder-metallurgy specimens of magnesium and magnesium alloys have been in use for some time. These include compaction and/or

sintering followed by extrusion. Machined chips or other finely divided magnesium or magnesium-alloy particles may be used for this process.

In addition, a recent method for direct extrusion of powder magnesium or magnesium alloys has been developed to a considerable extent. In this method, the powder is charged directly into the extrusion die chamber. The temperature of the powder is raised to the extrusion temperature in this chamber while the ram advances preparatory to extrusion. The properties obtained from material produced in this process are either comparable or superior to the properties of cast and extruded billets.

There are three advantages offered by powder-metallurgy compared to conventional methods: (1) control of grain size, (2) interference hardening, and (3) reduction or prevention of stress corrosion. In addition to these three benefits, it is also possible to raise the hot-short extrusion speed of an alloy by coextruding it with an alloy of a high hot-short extrusion speed. The same improvement in mechanical properties may also be expected

this case as in the case of the alloys coextruded for improved stress-corrosion properties.

CONTROL OF GRAIN SIZE

The compressive yield strength of magnesium and magnesium alloys is inversely related to the grain size. The grain size of magnesium alloys, on the other hand, is strongly influenced by the alloy gradient. The atomizing process for preparing powders for powder-metallurgy techniques is therefore particularly ideal.

This powder is prepared by atomizing a molten stream of the alloy desired in a jet of cool gas which solidifies and chills the alloy in extremely small particles. This results in the steep concentration gradient of a highly cored structure. When these particles are subsequently extruded, the resulting structure retains the steep gradient of the particles, resulting in a fine grain size. The properties of material thus prepared are considerably superior to those of material prepared by conventional techniques. The improved properties are destroyed, however, by solution heat treatment.

INTERFERENCE HARDENING

Powder metallurgy is frequently used to prepare alloys which cannot be prepared by conventional melting practice. For example, aluminum and zirconium coprecipitate from molten magnesium alloys, but a magnesium-zirconium alloy powder may be extruded with aluminum powder to form a magnesium-zirconium-aluminum alloy. This results in a finely divided zirconium-aluminum precipitate which does not dissolve upon heat treatment or extended aging. This alloy, therefore, retains its properties even for extended times at elevated temperatures. The improvement in properties obtained by this method is often referred to as interference hardening. The technique is applicable also to aluminum-manganese alloys and other alloys wherein the solubility of one constituent is limited by the addition of the other.

PREVENTING STRESS CORROSION

Many high-strength magnesium alloys are highly susceptible to stress corrosion. These alloys may be protected from corrosion and stress failure either by the application of an electrical potential or by the use of an anodic couple. This same protection can be afforded by coextruding a nonsusceptible magnesium alloy with a susceptible magnesium alloy. In this manner, most of the high-strength magnesium extrusion alloys can be protected from stress corrosion. At the same time, a general improvement in mechanical properties is realized because of some interference hardening.

JOINING

Magnesium alloy parts can be joined by any of the present commercial methods. Gas-, arc-, and electric-resistance welding and riveting are common methods of joining magnesium parts, while brazing and adhesive bonding are also suitable.

WELDING

Gas welding is adaptable for joining most of the wrought and some of the cast magnesium alloys. Oxyacetylene, oxyhydrogen, and oxycarbohydrogen gases may be used.

Magnesium sheet, extrusions, forgings, sand castings, and permanent-mold castings may all be welded by the gas-shielded-arc method. In this type of welding, a tungsten electrode shielded by an inert gas, such as argon or helium, is employed. No flux is required for this type of welding.

Most magnesium sheet, extrusions, and casting alloys can be resistance spot welded. The best welds are obtained when alloys of the same composition are welded together, but reasonably good joints may be obtained when welding different alloys. When spot welding sheets of unequal thicknesses, the ratio of sheet thickness should be no greater than 2 to 1. The distance between spots should be at least 8 times the thickness of the sheet, and the recommended distance from the edge of the sheet is at least 4 times and preferably 6 times the sheet thickness.

SOLDERING

Magnesium alloys may be soldered provided there are no stresses involved in the structure. Soldering is ordinarily used only for filling imperfections in castings or sheet material. Two types of solders have been developed for use with magnesium alloys and are now commercially available. The first melts at 315°F and contains 10 percent tin, 30 percent zinc, and 60 percent cadmium. The second type melts at 500°F and contains 10 percent zinc and 90 percent cadmium. When magnesium is to be soldered, it should be preheated to approximately the melting point of the solder which is to be used.

MISCELLANEOUS BONDS

Several plastic and rubber compounds are commercially available for bonding magnesium surfaces. They are classified in two general categories: (1) thermal plastic or noncuring and (2) thermal setting or curing types. The selection of the type of bonding agent is dependent upon the application of the bonded structure.

MACHINABILITY

One of the principal properties of magnesium which makes it suitable for commercial applications is its excellent machinability resulting from the low resistance of magnesium to cutting. That property makes it acceptable for use where weight saving is not necessarily important but where a large amount of costly machining is required. Such parts, when made of magnesium, may be machined at exceptionally high speeds and with greater economy than would be encountered with most commonly used metals.

Machining tools of standard design as used for other metals may, in general, be employed for magnesium. Carbide tools are recommended for maximum efficiency, especially when extremely high cutting speeds are employed.

The power required to remove a given amount of magnesium is lower than that required for any other commercial metal. The power per cubic inch per minute for machining magnesium varies from 0.15 to 0.3 hp. For roughing operations, a cutting speed of 3,000 ft/min with a cut depth of 0.20 in. is possible. In the finishing operation, cutting speed may be as high as 9,000 ft/min with a cut depth of 0.030 in.

The primary purpose of cutting fluids used in machining magnesium is to reduce the fire hazard and to cool the work. Any improvements in surface finish and increased tool life are minor. A wide variety of mineral-oil cutting fluids will perform satisfactorily with magnesium. Water-soluble oils, oil-water emulsions, or water solutions should not be used on magnesium, as the presence of water intensifies chip fires. Although the fire hazard is normally not great under proper machining conditions, definite recommendations are available for proper practice and should be rigorously observed.

HEAT TREATMENT

The solid solubility of aluminum and zinc in magnesium increases with temperature. This is the basis of all magnesium heat treatment. Heat treatment is useful in alloys having from 6 to 13 percent aluminum and up to 3 percent zinc. Generally, however, aluminum is not added in amounts exceeding 9 or 10 percent. Alloys containing 8 percent aluminum or over develop greater hardness and higher yield strength when the solution heat treatment is followed by a precipitation or aging treatment. Heat-treated magnesium-aluminum-zinc alloys ordinarily are used for highly stressed application.

There are four types of heat treatment which may be given to these alloys, and they are usually designated in the trade as follows: (1) HT or T4—solution treatment; (2) HTA or T6—solution treatment and aged; (3) ACS—as cast and stabilized; (4) HTS or T61—heat treated and stabilized.

The solution heat treatment involves holding at temperatures in the range of 500° to 800°F, depending upon the exact alloy composition. The time required is about 16 to 20 hr. After the solution treatment, the alloys are cooled in a stream of air. The purpose of the solution heat treatment is to get as much as possible of the alloying ingredients into solid solution. Such a treatment improves the tensile strength, ductility, and toughness but does not change yield strength or hardness. The solution-heat-treated condition is the best for resistance to shock loading.

The aging heat treatment is conducted at 300° to 400°F after the above solution treatment. Aging, which usually lasts 12 to 16 hr, results in a further increase in the yield strength and hardness, with somewhat lower ductility. The solution-heat-treated and aged condition is best for applications requiring high yield strength and which are not subject to severe shock.

The stabilizing heat treatment is conducted in the temperature range 425° to 550°F for 2 to 6 hr. While this treatment may be referred to as an aging treatment, it is applied to as-cast metal as well in order to obtain rapidly a complete precipitation. Aging at this temperature produces almost complete stress relief and freedom from growth due to aging in service. When applied following the regular solution treatment, fair ductility is retained because of the coarse nature of the precipitate formed at the elevated temperature. Tests indicate that creep resistance is highest for material in the solution-treated and stabilized state.

Castings are cooled rapidly after the solution treatment at the moment the castings are removed from the furnace by directing a stream of moving air onto them. Drastic quenching by plunging the casting into a cold-water bath should be avoided because this practice produces severe residual stresses. Proper heat treatment of castings is mandatory if satisfactory strength and ductility are to be obtained.

No specific time-temperature recommendations have been made in the foregoing. The heat-treatment cycle for any particular alloy application must be determined by the com-

position of the alloy used and the shape of the piece, as well as the stresses to which it is to be subjected. The literature is replete with specific recommendations for the heat treatment of any particular commercial alloy.

CORROSION BEHAVIOR

Unalloyed magnesium has good resistance to atmospheric exposure and to attack by alkalis, chromic and hydrofluoric acids, and organic chemicals, such as hydrocarbons, aldehydes, alcohols, phenols, amines, esters, and most oils.

Magnesium alloys have vastly different rates of corrosion, depending upon the alloy content and type of exposure. A study of the effects of nonmetallic and alkaline metal impurities on the corrosion characteristics of high-purity magnesium in a room-temperature aqueous solution of 3-percent NaCl indicates that sodium, calcium, and possibly carbon are detrimental to the corrosion properties. Lithium, barium, strontium, potassium, silicon, chlorine, nitrogen, oxygen, and phosphorus, present in small quantities, have no detectable effects provided the magnesium is pure. The same may not be true, however, if iron is present as an impurity in the magnesium. It is desirable to limit the iron content of magnesium to 60 ppm. The maximum corrosion rate occurs at approximately 150 ppm.

Thermal history has a very pronounced effect on the corrosion rate of high-purity magnesium alloys containing iron. An alloy containing approximately 150 ppm of iron offered a twentyfold decrease in corrosion rate when solution treated at 1100°F for 16 hr. In identical alloys, specimens cooled very rapidly from liquid to solid have corrosion rates considerably lower than that for specimens cooled slowly.

The magnesium used for the above tests was prepared by a special multiple-distillation process and was at least 99.998 percent magnesium. Tests in distilled water (both at 212°F and 120°F) conducted at Battelle showed the corrosion resistance of the multiply-distilled metal under these conditions to be inferior to that of commercial purity metal. No magnesium or magnesium alloy yet developed has suitable corrosion resistance in water at temperatures much above room temperature, and the highest purity metal obtainable is at least no better than that now commercially available.

The most serious problem concerning magnesium corrosion in common applications is encountered in atmospheres of high salt concentration of the type encountered around sea coasts. The problem may be easily overcome in ordinary applications by any one of several methods of surface protection, such as painting, electrochemical treatments, or chemical treatments.

The corrosion resistance of the magnesium-lithium binary alloys has not been investigated very extensively. The alloys, in general, have poorer resistance to laboratory salt-water immersion tests. However, some binary Mg-Li alloys appear to have corrosion resistance comparable with that of Dow M-1 alloy. Table 1.12.10 presents the results of some laboratory tests.

LIQUID-METAL PROPERTIES

THE RESISTANCE OF SOLID MAGNESIUM TO ATTACK BY LIQUID METALS

Magnesium offers very little resistance to attack by liquid metals, because the majority of metals whose melting points are lower than magnesium are capable of dissolving it. Magnesium does, however, have a limited resistance to attack by sodium and sodium-potassium alloys in the temperature range of 120° to 300°F.

Table 1.12.10—Corrosion Resistance of Mg-Li Base Alloys
Compared With That of Commercial ASTM Alloy M-1

Nominal composition, wt-%				Average weight loss, mg/(cm ²)(day)
Mn	Li	Zn	Mg	
1.26*			Balance	0.62
	2.0		Balance	4.92
	4.0		Balance	4.44
	9.3		Balance	0.77
	11.0		Balance	.57
	9.0	4	Balance	2.81
	10.6	4	Balance	2.83

*Dow M-1 Alloy

RESISTANCE OF OTHER METALS TO ATTACK BY LIQUID MAGNESIUM

Cast iron and low-carbon steel offer good resistance to attack by liquid magnesium at the melting point of magnesium and offer a limited resistance up to 1470°F. High-chromium stainless steels offer somewhat better resistance than do cast iron and low-carbon steels. Austenitic stainless steel is attacked severely by magnesium at the melting point of the latter. Beryllium offers fairly good resistance up to 1470°F. Titanium resists attack quite well up to 1380°F; it is fairly resistant up to 1560°F.

The metals which offer the highest resistance to attack by liquid magnesium, listed in order of decreasing resistance, are: niobium, tungsten, tantalum, molybdenum, and chromium.

Aluminum, silver, gold, barium, bismuth, calcium, cadmium, cobalt, copper, gallium, lithium, manganese, nickel, lead, palladium, platinum, antimony, silicon, tin, thallium, and zinc all offer extremely poor resistance to attack by liquid magnesium. This lack of resistance is due primarily to the ability of those elements to form solid solutions with magnesium.

PROTECTIVE TECHNIQUES

Although magnesium and magnesium alloys have good resistance to corrosion in most atmospheres, the protective film that is formed does not retain a metallic appearance but changes gradually to dark gray. The resistance of magnesium to tarnish can be improved greatly by creating supplementary coatings on the surface with either chemical or electrochemical treatment and in either acid or alkaline solutions.

The acid baths used in chemical treatments are normally dichromate solutions with or without additions of sulfates, phosphates, chlorides, or nitrates. The films which are formed are usually amorphous mixtures of hydrated chromium and magnesium oxides. In strongly alkaline solutions, a magnesium hydroxide film is formed which may contain traces of other agents that are added to the bath.

BRIGHT PICKLE

Magnesium is bright after pickling in aqueous solutions of many acids. However, the film which is formed does not resist tarnish. An acid bath that produces good resistance

to tarnish in all commercial magnesium alloys contains 18 percent chromic acid, 4 percent calcium nitrate, and 0.25 percent magnesium fluoride. Immersion in this solution, maintained at 68° to 86°F for from $\frac{1}{2}$ to 5 min must be followed quickly by a dip rinse in a bath containing 5 percent sodium metasilicate or sodium carbonate.

This bright-pickle treatment provides a thin, clear film that is quite resistant to the normal atmosphere. Parts given this treatment may be handled extensively without tarnishing, and clear or pigmented organic coatings may be applied to it.

CHROME PICKLE—TYPE 1

This is the most widely used chemical treatment for commercial magnesium alloys. The work material is dipped for $\frac{1}{2}$ to 2 min in a bath consisting of 180 gm/l of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 187 ml/l concentrated HNO_3 . The bath is maintained at room temperature. Parts are suspended in air for 5 sec after removal from the bath before being rinsed in cold then hot water. This treatment is described extensively in technical publications.

SEALED CHROME PICKLE—TYPE 2

This treatment consists of two steps, the first being the room-temperature chrome pickle described previously. The part is then sealed by holding for 30 min in a boiling solution that contains 100 to 150 gm/l $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

DICHROMATE—TYPE 3

The best resistance to corrosion and the best adhesion of paint are imparted to commercial magnesium alloys by the dichromate pickle. This treatment also is applied in two steps, as quoted from the 1948 edition of the ASM Metals Handbook:

Step 1. Dip parts for 5 min in a cold, aqueous solution containing 15 to 20 percent by weight of hydrofluoric acid; rinse in cold water.

Step 2. Boil parts 30 min in an aqueous solution containing 100 to 150 gm/l $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, saturated with either magnesium fluoride or calcium fluoride. Rinse and dry.

All three chromate treatments may be applied to any one of the commercial alloys. The dichromate treatment does not, however, produce a dark coating on M-1 alloy. Exposures of alloys at Kure Beach, North Carolina, have shown that the coatings produced by these treatments retain surface appearance somewhat better than the surface appearance of bare magnesium. However, after two years of exposure at a station located 800 ft from the ocean, no improvement of mechanical properties over uncoated magnesium alloys was noted.

ACID ANODIZING

Protective coatings may be applied to magnesium by making it the anode in certain acid or alkaline solutions. The baths used are similar to those used normally for direct chemical treatment, the application of current simply reducing the required time and temperature. On the other hand, the throwing power of these baths is often insufficient to coat complicated parts completely, and such baths are often more expensive to operate.

CAUSTIC ANODIZING

Some coatings that are produced by anodic oxidation in strongly alkaline solutions are more resistant to corrosion in aqueous solutions than are coatings formed in chromate baths. This treatment requires the application of either direct or alternating current to the magnesium for 15 to 25 min at a current density of 10 to 25 amp/sq ft. The bath, 25 percent NaOH, 7 percent diethylene glycol and 0.2 percent sodium oxalate, is operated

at 165° to 175°C. The coating formed is a hard compact $\text{Mg}(\text{OH})_2$. It is normally of a neutral, light-gray shade, and is applicable to all commercial magnesium alloys.

ELECTROPLATING

No commercially acceptable electroplating process has been developed for magnesium, but results of recent research indicate that satisfactory methods may be available shortly.

METALLOGRAPHY

In preparing specimens for microscopic examination, it should be remembered that magnesium and magnesium alloys are relatively soft metals. Therefore, the specimen should be removed from its surroundings with the least possible rough handling, since cold work may alter the microstructure and complicate the subsequent examination. Conventional mounting, grinding, and polishing techniques are applicable to magnesium and magnesium alloys with the reservation that care must be exercised at all times to prevent working of the metal. In general, this means the use of slow speeds, light pressures, and a lubricant in all steps. Final polishing must be done with distilled water, using Merck's USP heavy-grade magnesium oxide as an abrasive. The specimen should be immediately immersed in hot-flowing distilled water after polishing, and blown dry.

Magnesium and magnesium alloys can be polished electrolytically by Jacquet's method to yield excellent surfaces free from flowed metal. The sample is ground, as for mechanical polishing, through at least 300 abrasive paper. The solution used consists of 375 ml of orthophosphoric acid, density 1.71, and 625 ml of ethyl alcohol, 95 percent by volume. The current density required is 0.5 to 1.0 amp/sq cm at a potential of 1.5 volts. The duration of electrolysis is from 3 min to 1 hr depending upon the extent of previous mechanical preparation.

The chemical activity of magnesium does not permit the use of strong inorganic acids for etching except in weak solutions. Organic acids in aqueous solutions, inorganic acids in organic solutions, aqueous salt solutions and combinations of these are the commonly used etching solutions. The ASM Metals Handbook contains a complete list of useful etchants.

SELECTED READING LIST*

PREPARATION OF HIGH PURITY MAGNESIUM AND A STUDY OF THE EFFECT OF NON-METALLIC AND ALKALI METAL IMPURITIES ON THE CORROSION CHARACTERISTICS OF PURE MAGNESIUM, Dow Chemical Company, A Series of Reports to the AEC Beginning with First Quarterly Report, March 6, 1950, and Continuing through May 31, 1952, COO-13, COO-14, COO-15, COO-21, COO-43, COO-47, COO-78, COO-85, and COO-88, No dates.

ROOM AND ELEVATED TEMPERATURE PROPERTIES OF POWDER EXTRUDED MAGNESIUM ALLOYS CONTAINING ALUMINUM, BERYLLIUM, AND ZIRCONIUM, Dow Chemical Company, A Series of Reports to the AEC Beginning With First Quarterly Report September, 1950, and continuing through April 30, 1951, COO-16, COO-20, COO-42, and COO-48, No dates.

THE EFFECTS OF TEMPERATURE ON THE MECHANICAL PROPERTIES OF MAGNESIUM ALLOYS, Battelle Memorial Institute, C. M. Craighead, et al., R-146, 223 pp, April 29, 1949.

MAGNESIUM, W. H. Gross, American Society for Metals, Cleveland, Ohio, 258 pp, 1949.

MAGNESIUM, ASM EDUCATIONAL LECTURE, American Society for Metals, Cleveland, Ohio, 265 pp, 1946.

MAGNESIUM AND MAGNESIUM ALLOYS, ASM Metals Handbook, American Society for Metals, Cleveland, Ohio, 1946.

*Data books on magnesium and its alloys, their fabrication and heat treatment are available upon request from the Aluminum Company of America, the American Magnesium Corporation, and the Dow Chemical Company.

CHAPTER 1.13

Molybdenum and Its Alloys

R. M. Parke,* J. A. Van Echo, W. E. Few, and L. E. Olds

REACTOR APPLICATION

Of the 10 refractory metals that are liquid only above 3500°F, molybdenum is the most available and the art of fabricating it is in the most advanced state. It is one of the metals expected to serve in reactors as a material of construction under high stress at temperatures above 1600°F. This expectation will be limited to use in nonoxidizing atmospheres until methods for reducing the oxidation rate are perfected.

AVAILABILITY AND COST

Under the impetus of war, the production of molybdenum in this country reached an all-time high of 31,400 metric tons in 1943. U. S. production has supplied to date and probably

Table 1.13.1 — World and U. S. Production of Molybdenum Metal

Year	Production, metric tons	
	World	U. S.
1938	16,400	15,103
1939	15,200	13,755
1940	17,200	15,564
1941	20,300	18,309
1942	29,000	25,829
1943	31,400	27,972
1944	21,400	17,545
1945	15,900	13,972
1946	10,800	8,264
1947	14,000	12,268
1948	13,600	12,114
1949	11,500	10,219
1950	14,400	12,918

currently supplies 90 percent of the world's need for this metal, as shown in Table 1.13.1.

Molybdenum is obtainable principally as metal of 99.9+ percent purity, as oxide (MoO_3), as sulfide (MoS_2), and as ferromolybdenum. The metal is supplied in the form of powder, sheet (minimum thickness 0.003 in.), plates, wire (minimum diameter 0.003 in.), bars,

* General Electric Co., Knolls Laboratory.

rod, forgings ($2\frac{1}{2}$ in. or less in diameter), and seamless tubing (minimum outside diameter $\frac{1}{16}$ in.).

A few manufacturers have experience in the welding, forging, swaging, drawing, stamping, punching, shearing, spinning, machining, grinding, brazing, and spraying of molybdenum, so that complex fabricated shapes may be obtained on special order.

Molybdenum is obtainable in large rectangular or cylindrical bodies, made by the powder-metallurgy process (hydrostatically pressed and sintered in hydrogen), up to 5 ft in length and weighing as much as 1000 lb.

Molybdenum is also being produced by an arc-melting process and ingots of 1000 lb have been cast.

Typical current prices for molybdenum sheet, wire, and rod in small quantities are as follows:

Sheet, 0.187 in. thick by 3 in. wide	\$30/kg
Wire, 30 mils	\$15/kg
Swaged rod, 500 mils	\$15/kg
Powder, 80 mesh	\$25/kg
Seamless tubing, 0.5 in. OD, 0.090 in. wall	\$6/linear in. or \$139/kg
Seamless tubing, $\frac{1}{16}$ in. OD, 0.010 in. wall	\$1/linear in. or \$1650/kg

EXTRACTION AND PURIFICATION

The principal source of molybdenum is the mineral molybdenite (MoS_2). Molybdenite, in the form of an ore concentrate containing about 5 percent silica and smaller amounts of other elements, is converted to an impure (technical grade) molybdenum trioxide by heating in air in Herreshof furnaces. In this process, temperatures are kept low (1100°F or lower) to avoid loss by vaporization of MoO_3 . Pure molybdenum oxide is made by volatilizing the technical-grade oxide at 1800°F and collecting the condensate. This product is 99.97+ percent molybdenum oxide. The principal impurity is silica. The pure oxide may be converted to molybdenum metal powder by reduction with hydrogen.

Sometimes further purification is attained by dissolving the pure oxide in NH_4OH , precipitating ammonium molybdate by slightly acidifying with HCl , heating ammonium molybdate to 1400°F to reduce to MoO_3 and finally reducing MoO_3 to Mo with hydrogen at 2200°F . By these methods, molybdenum powder of 99.95+ percent purity is obtainable. The metallic impurities are iron, nickel, chromium, copper, silicon, aluminum, magnesium, and manganese. Nonmetallic impurities include hydrogen, nitrogen, oxygen, and carbon.

PHYSICAL AND CHEMICAL CONSTANTS

GENERAL

Table 1.13.2 lists some of the physical and chemical constants of molybdenum.

CRYSTALLOGRAPHY

CRYSTAL STRUCTURE

The crystal structure is body-centered cubic at room temperature with a lattice parameter of 3.1466 Å.

No anomalies in electrical or thermal properties have been observed which suggest a transformation to another crystal form.

The slip plane is (110) and slip direction [111] in single crystals both at room temperature and at 1000°C .

Table 1.13.2—Physical and Chemical Constants of Molybdenum

Thermal-neutron-absorption cross section, barns/atom	2.4 ± 0.2
Density,* gm/cm ³	
Powder, bulk density	3.0
Cold-pressed bar	6.0
Sintered bar	9.8
Sintered bar, worked to sheet or wire	≤10.3
Arc cast	10.2
Melting point, °C	2622 ± 10
Boiling point, °C	4804
Vapor pressure, μ	
1954°C	0.01
2125°C	0.1
2324°C	1.0
2568°C	10.0
2622°C (melting point)	15.7
Heat of fusion, cal/gm	70
Heat of vaporization, cal/gm	1625
Specific heat,† cal/(gm)(°C)	
-257°C	0.0004
-181.5°C	.0300
0°C	.0589
100°C	.0650
475°C	.0750
Enthalpy (H _T - H _{25°C}), cal/mole	
127°C	610
527°C	3105
927°C	5825
1327°C	8740
Entropy (S _T - S _{25°C}), cal/(mole)(°C)	
127°C	1.76
527°C	6.07
927°C	8.82
1327°C	10.91
Coefficient of linear thermal expansion, per °C	
-173°C	2.8 × 10 ⁻⁶
-23°C	5.0 × 10 ⁻⁶
27°C	5.1 × 10 ⁻⁶
500°C	5.1 × 10 ⁻⁶
1000°C	5.5 × 10 ⁻⁶
1500°C	6.2 × 10 ⁻⁶
2000°C	7.2 × 10 ⁻⁶
Thermal conductivity,‡ cal/(sec)(cm)(°C)	
-183°C	0.44
-78°C	.33
0°C	.32
1473°C	.26
2173°C	.17
Electrical resistivity, μohm-cm	
0°C	5.17
27°C	5.78
727°C	23.9
1127°C	35.2
1527°C	47.2
1927°C	59.5
2327°C	71.8
2622°C	81.4
Allotropy	None discovered

* Gm/cm³ × 62.43 = lb/cu ft

† Cal/(gm)(°C) × 1.0 = Btu/(lb)(°F)

‡ Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

DEFORMATION TEXTURES

The preferred orientations after working are, in general, typical for body-centered cubic metals. Drawn wire has a [110] texture, which is retained upon recrystallization. The predominant orientation in both straight-rolled and cross-rolled molybdenum is (100)[110].

Arc-melted molybdenum in the as-cast state has a preferred orientation in which [100] is perpendicular to the isotherms during cooling of the ingot and parallel to the long axis of the grains.

The predominant texture of recrystallized cross-rolled sheet is (100)[110].

HEALTH HAZARDS

An exhaustive study of the physiological effect of molybdenum on humans had not been made and there is no evidence to suggest a pressing need for such a study. There are no known reports of troublesome symptoms attributable to molybdenum in personnel working under normal conditions for periods of several years in the mining or conversion of molybdenum or fabrication of the metal.

HANDLING AND STORAGE

Molybdenum in consolidated form (i.e., in rod, sheet, or wire) is a stable material tarnishing very slowly in ordinary atmosphere and requiring no special care in handling or storage. In powder form, it slowly picks up oxygen from the air. Such oxidized powder might not be fabricable to rods or sheet, but the original properties may be recovered by heating to 2000° to 2200°F in flowing hydrogen to remove the oxygen.

MECHANICAL PROPERTIES

TENSILE AND COMPRESSION PROPERTIES

The tensile properties of molybdenum are dependent upon the amount of hot and cold work, the amount, kind, and distribution of impurities, the annealing temperature, and very probably the interactions between these variables.

In general, the yield and tensile strengths (in the direction of working) are increased as the amount of working increases. The yield and tensile strengths are decreased with an increase in annealing temperature, but annealing above 2500°F may (although not always) cause low ductility at room temperature. This type of embrittlement is usually accompanied by a change from a fibrous structure to a recrystallized (equiaxed grain) structure. It appears that purity is a significant determinant of response to annealing, but the particular elements responsible for the recrystallization embrittlement and the concomitant effect of working have not yet been determined.

Table 1.13.3 gives the room-temperature tensile properties of powder-metallurgy molybdenum.

Table 1.13.4 gives the room-temperature tensile properties of arc-melted molybdenum after hot rolling and after hot rolling and subsequent annealing.

The effect of test temperature on tensile properties of arc-cast and powder-metallurgy molybdenum is shown in Figs. 1.13.1 and 1.13.2.

The effect of test temperature on notched-bar tensile properties of arc-cast and powder-metallurgy molybdenum is shown in Figs. 1.13.3 and 1.13.4.

**Table 1.13.3—Mechanical Properties of Powder-metallurgy
Molybdenum Sheet at Room Temperature**

Yield strength	65,000 lb/sq in.
Tensile strength	82,000 lb/sq in.*
Elongation	20 percent*
Vickers hardness	215
Young's modulus	47.0×10^6 lb/sq in.†

* See Tables 1.13.11 and 1.13.12 for values at elevated temperatures

† See text that follows under Elastic Constants for values at elevated temperatures

Table 1.13.4—Mechanical Properties of Arc-cast, Hot-rolled Molybdenum at Room Temperature

Annealing temperature, °F	Yield point, lb/sq in.	Tensile strength, lb/sq in.	Elongation, %	Reduction of area, %	Vickers hardness	Young's modulus, 10^6 lb/sq in.	Modulus of rigidity, 10^6 lb/sq in.	Poisson's ratio
Hot rolled	99,800	101,100	32	60.9	225	46.0	17.4	0.324
1700	...	91,700	39	59.2
1900	84,700	90,600	41	65.7
2100	54,100	73,100	53	64.2	187
2200	50,100	73,600	55	55.6	187

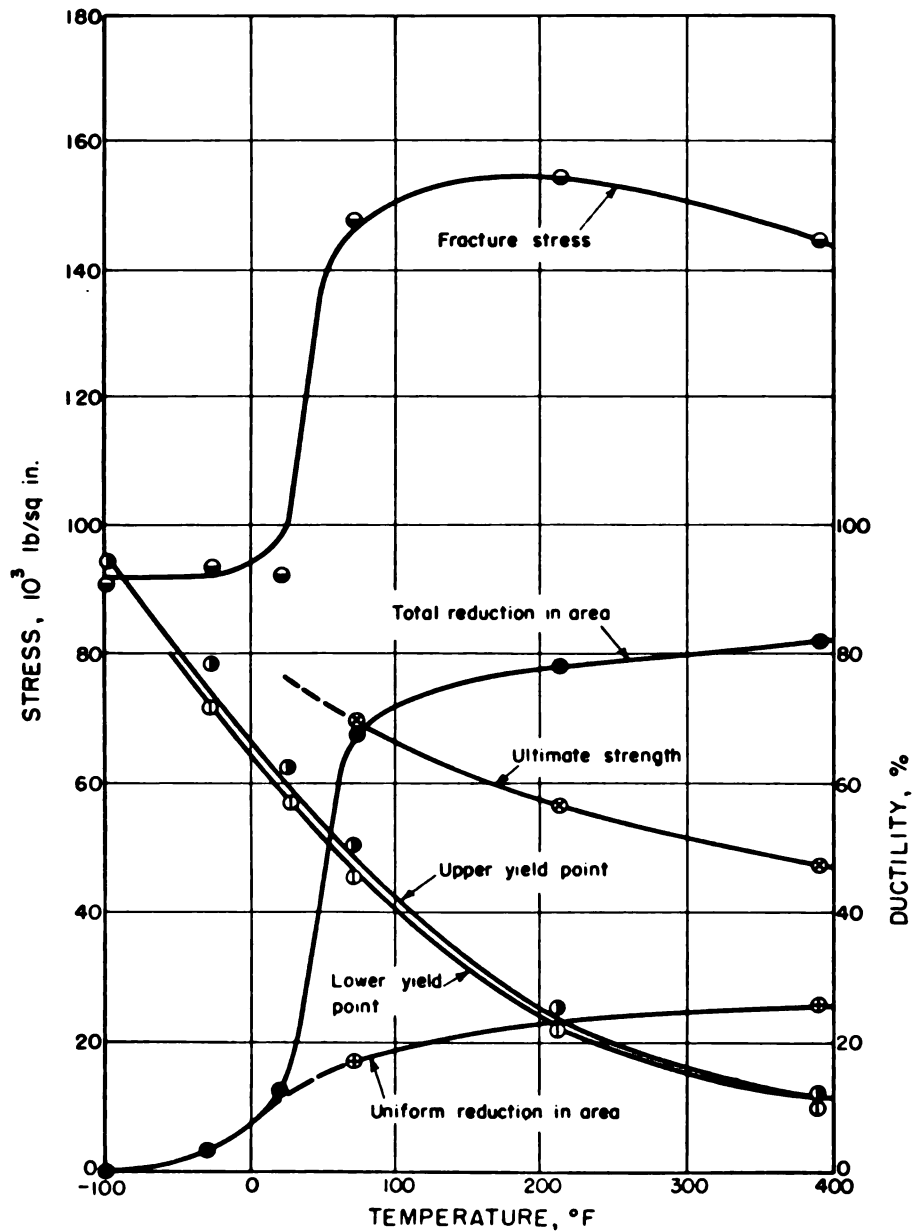


Fig. 1.13.1—Effect of Test Temperature on Tensile Properties of Arc-cast Molybdenum. Strain Rate, $2.8 \times 10^{-4}/\text{sec}$. Reprinted from J. H. Bechtold and H. Scott, Mechanical Properties of Arc-Cast and Powder Metallurgy Molybdenum, J. Electrochem. Soc., 1951.

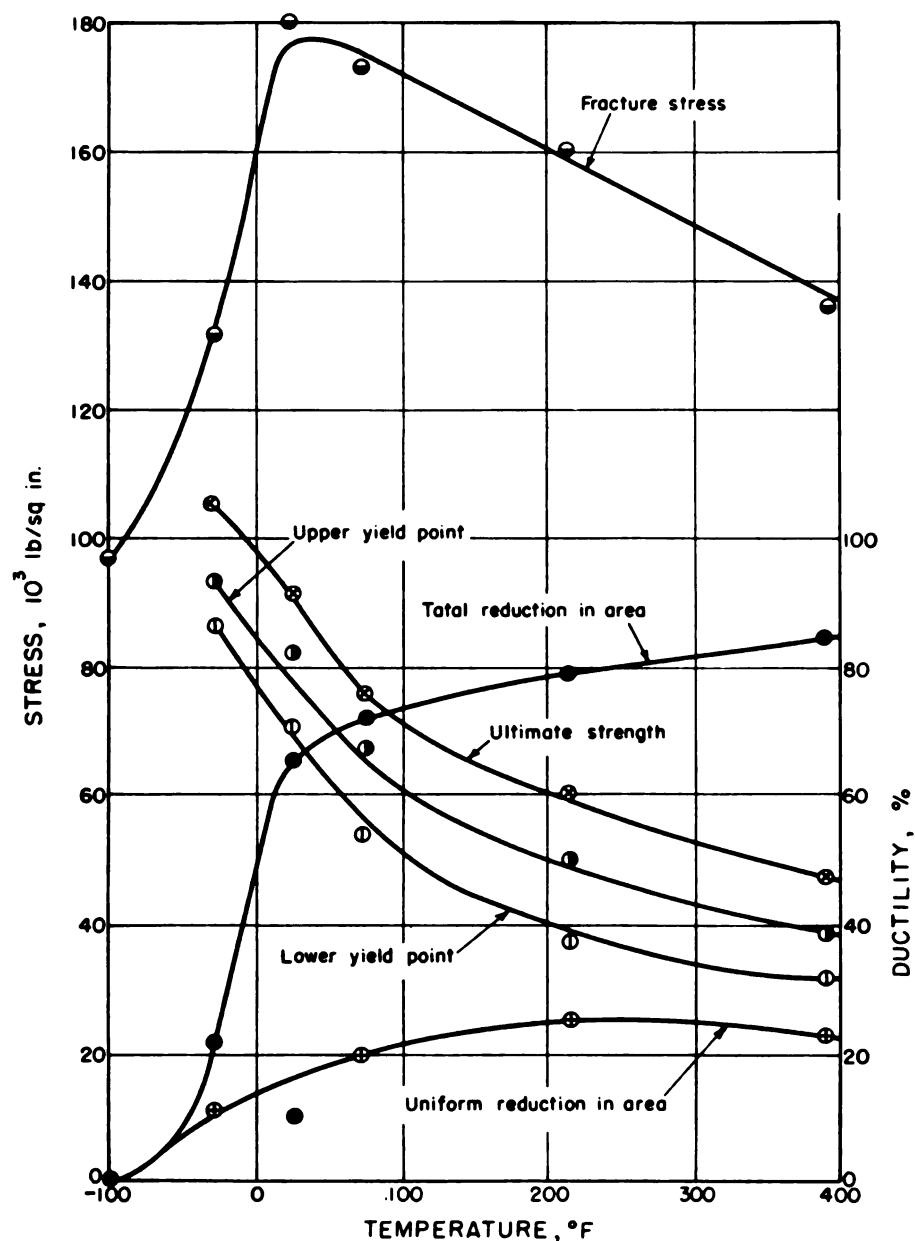


Fig. 1.13.2—The Effect of Test Temperature on the Tensile Properties of Powder-metallurgy Molybdenum. Strain Rate, $2.8 \times 10^{-4}/\text{sec.}$ Reprinted from J. H. Bechtold and H. Scott, Mechanical Properties of Arc-Cast and Powder Metallurgy Molybdenum, J. Electrochem. Soc., 1951.

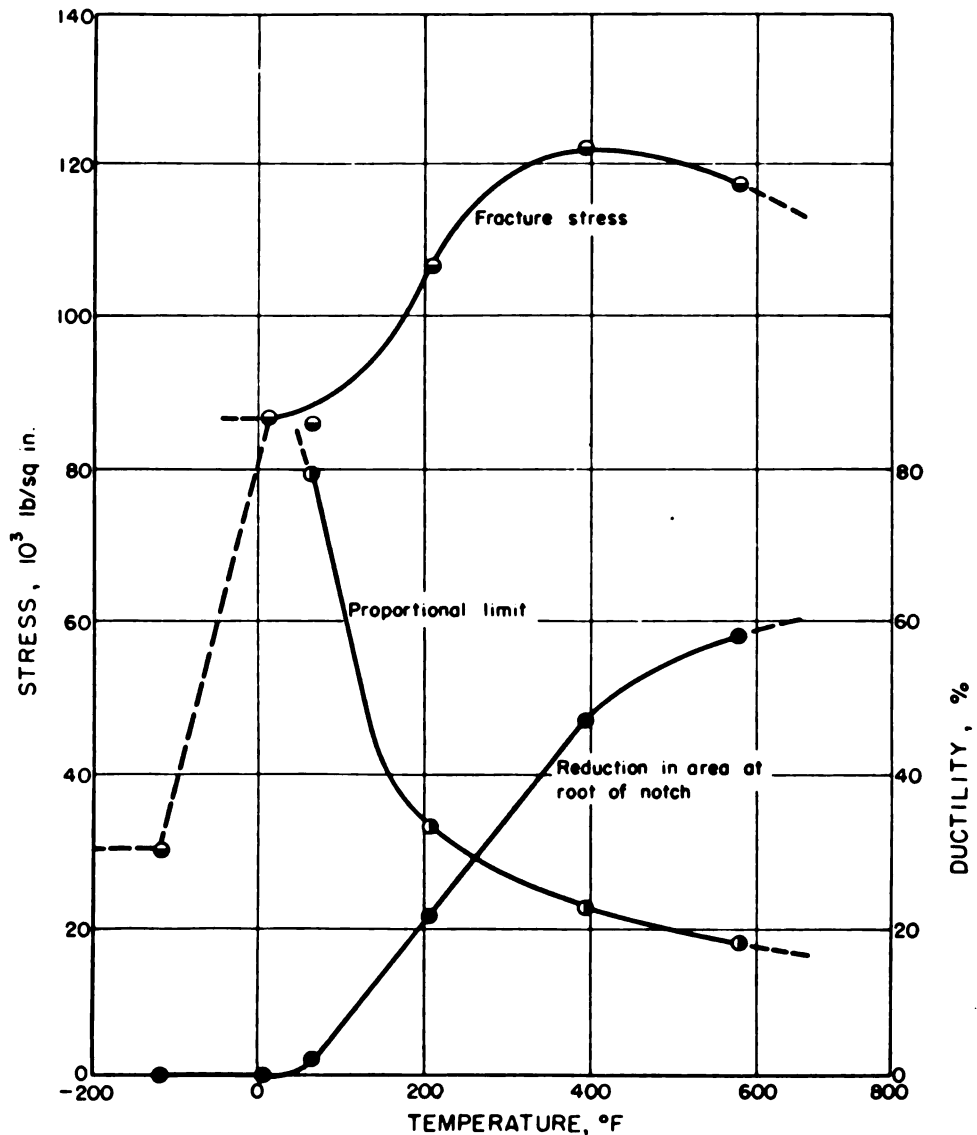


Fig. 1.13.3—The Effect of Test Temperature on the Notched-bar Tensile Properties of Arc-cast Molybdenum. Notch Concentration Factor, $K_T = 3.1$. Reprinted from J. H. Bechtold and H. Scott, *Mechanical Properties of Arc-Cast and Powder Metallurgy Molybdenum*, J. Electrochem. Soc., 1951.

ELASTIC CONSTANTS

The Young's modulus of molybdenum at room temperature is 48×10^6 lb/sq in. and decreases approximately 350,000 lb/sq in. per 100°F up to 1100°F. At 1300°F it is 43×10^6 lb/sq in. and at 1500° and 1600°F it is 41.5×10^6 and 39.9×10^6 lb/sq in., respectively.

The modulus of rigidity is 17×10^6 lb/sq in. at room temperature and decreases approximately 130,000 lb/sq in. per 100°F up to 1100°F.

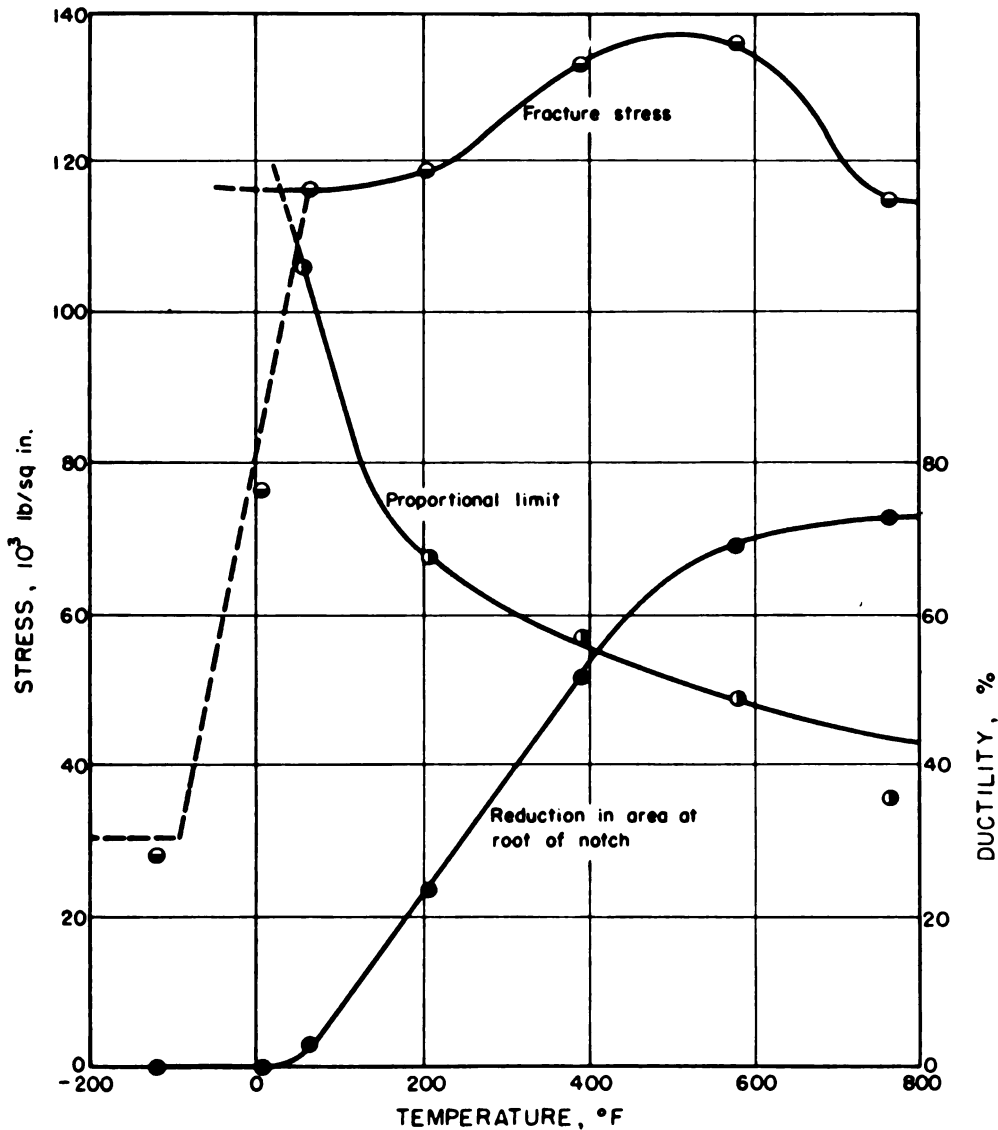


Fig. 1.13.4—The Effect of Test Temperature on the Notched-bar Tensile Properties of Powder-metallurgy Molybdenum. Notch Concentration Factor, $K_T = 3.1$. Reprinted from J. H. Bechtold and H. Scott, *Mechanical Properties of Arc-Cast and Powder Metallurgy Molybdenum*, J. Electrochem. Soc., 1951.

DIRECTIONAL PROPERTIES

The directional properties of arc-cast molybdenum in the hot-rolled-annealed and in the cold-rolled condition are given in Tables 1.13.5 and 1.13.6.

Preliminary data indicate that the ratio of fatigue strength to tensile strength in molybdenum is relatively high, possibly as high as 65 percent.

Table 1.13.5—Directional Properties of Arc-cast, Hot-rolled, Annealed Molybdenum Sheet at Room Temperature

(Metal Progress, August 1950)

No.*	Direc- tion†	Yield point, lb/sq in.	Tensile strength, lb/sq in.	Elong- gation, %	180° Bend over T‡	
					Cold	Hot
0.050-in. sheet, annealed at 1850°F						
SR-2	0°	101,700	106,300	22	OK	
	90°	116,300	117,200	18	NG	
	45°				OK	
CR-2	0°	102,800	107,800	22	OK	
	90°	109,600	110,900	14	NG	OK
	45°				OK	
0.020-in. sheet, annealed at 1800°F						
SR-1	0°	99,500	105,400	12	NG	OK
	90°	112,900	115,400	8	NG	OK
	45°				NG	OK
CR-1	0°	104,700	111,400	14	OK	OK
	90°	121,600	122,000	8	NG	OK
	45°				NG	OK
SR-2	0°	103,600	109,000	11	NG	OK
	90°	114,900	117,300	13	NG	OK
	45°				NG	OK
CR-2	0°	108,900	114,100	14	OK	OK
	90°	123,500	125,100	12	NG	OK
	45°				NG	OK
0.013-in. sheet, annealed at 1800°F						
SR-1	0°	102,400	116,500	14	OK	
	90°	116,000	118,400	8	NG	OK
	45°				OK	
CR-1	0°	106,400	110,100	11	OK	
	90°	107,000	108,500	10	NG	OK
	45°				OK	
SR-2	0°	108,300	112,700	14	OK	
	90°		124,000		NG	OK
CR-2	0°	107,000	112,500	10	OK	
	90°	120,000	121,000		NG	OK

* SR, straight rolled; CR, cross rolled

† Direction of the test bar in relation to final rolling

‡ Thickness

Table 1.13.6—Directional Properties of Arc-cast Cold-rolled Molybdenum Sheet* at Room Temperature

(Metal Progress, August 1950)

Annealing temperature, °F	Yield point, lb/sq in.	Tensile strength, lb/sq in.	Elongation, %
Longitudinal			
Cold-rolled	151,800	154,300	5
1600	126,500	131,500	12
1700	121,500	124,500	10
1800	111,000	117,300	13
1900	98,000	105,500	17
2000	74,400	88,800	29
2100	73,100	91,300	28
2200	75,500	90,600	26
2300	81,800	88,400	26
2400	75,400	78,800	39
Transverse			
1600	130,200	132,100	3
1700	120,900	120,900	2
1800	...	123,400	2
1900	113,700	114,700	8
2000	81,200	93,500	17
2100	86,700	91,500	16
2200	82,800	91,100	17
2300	55,000	89,400	16
2400	76,800	83,200	22

* Tested in 1-in. gauge length, ½ inch wide; all material was cold rolled from 0.052- to 0.020-in. thickness

ELEVATED-TEMPERATURE PROPERTIES

For molybdenum from different sources, the creep-rupture and tensile properties at elevated temperatures display considerable variation. There also appears to be considerable variation in such properties among different lots of molybdenum from the same source. This is also probably true with molybdenum-base alloys, although less is known about the alloys since they are relatively new. This variation in properties of molybdenum is attributed to a number of factors, including (1) fabrication history, (2) amount and distribution of impurities, and (3) testing procedures. The fabrication history is a principal factor since it in turn affects the amount of cold work, grain size and shape, preferred orientation, and concentrations of such impurities such as oxygen, nitrogen, and hydrogen. Accordingly, the creep-rupture and tensile properties presented here are typical rather than absolute values from any particular source.

CREEP-RUPTURE PROPERTIES OF MOLYBDENUM

Tables 1.13.7 and 1.13.8 show the creep-rupture properties of recrystallized arc-cast and powder-metallurgy molybdenum at temperatures of 1600°, 1800°, and 2000°F.

The ductility of molybdenum is intimately related to the oxygen content of the material. A low ductility at elevated temperatures is not necessarily characteristic of molybdenum but rather of the test atmosphere. Specimens run in a reducing (H₂) atmosphere show greater ductility than those run in vacuum.

Table 1.13.7—Creep-rupture Properties of Recrystallized Arc-cast Molybdenum*

Stress, lb/sq in.	Rupture time, hr	Elongation, %	Reduction of area, %	Approximate minimum creep rate, %/hr
1600°F in vacuum				
32,500	0.2	47.1	84.0	...
25,000	9.6	60.8	85.0	...
20,000	70.4	64.7	88.0	0.40
18,500	110.4	60.5	82.3	.06
1600°F in hydrogen atmosphere				
25,000	3.8	55.4	87.7	...
20,000	31.7	60.3	88.5	0.85
16,500	135.7	65.5	90.8	.21
1800°F in vacuum				
20,000	2.0	70.3	85.0	...
15,000	14.0	41.3	81.0	...
12,500	57.7	40.6	81.0	0.50
10,000	482.0	17.4	48.9	.013
1800°F in hydrogen atmosphere				
20,000	1.3	54.2	87.1	...
15,000	11.2	72.1	93.4	...
12,500	34.4	62.9	92.9	...
10,000	146.8	79.6	91.4	0.14
2000°F in vacuum				
15,000	0.9	74.0	67.0	...
12,500	15.1	30.5	86.0	1.0
10,000	103.5	50.0	78.0	0.11
8,500	1410.0	17.0	25.5	.0067
2000°F in hydrogen atmosphere				
12,500	2.4	72.0	92.0	...
10,000	8.6	76.3	93.5	...
8,500	27.9	75.6	93.7	0.75
6,000	258.9	92.5	95.2	.065

*This material was made from powder by the arc-casting method. After casting, the billet was forged and rolled to $\frac{1}{2}$ -in.-diameter bar. The rolling was done at a temperature below the recrystallization temperature of molybdenum resulting in a cold-worked structure. Chemical analysis showed 0.067 percent carbon. Specimens ($\frac{1}{4}$ -in. diameter by $1\frac{1}{4}$ -in. long gauge section) were machined from the $\frac{1}{2}$ -in. bar. Recrystallizing treatment was for 1 hr at 2000°F

Table 1.13.8—Creep-rupture Properties of Recrystallized Powder-metallurgy Molybdenum Under Vacuum*

Stress, lb/sq in.	Rupture time, hr	Elongation, %	Reduction of area, %	Approximate minimum creep rate, %/hr
1600°F				
20,000	7.3	62.0	92.0	...
17,000	38.1	78.6	91.0	...
15,000	93.6	59.8	90.0	0.20
13,500	327.7	65.3	88.4	.073
1800°F				
15,000	3.8	50.4	72.6	...
12,000	18.5	35.9	38.6	...
10,000	157.7	59.2	78.9	0.10
8,500	724.4	47.5	73.7	.027
2000°F				
10,000	2.4	19.0	21.2	...
8,000	9.2	13.6	11.9	...
6,000	84.9	6.7	10.4	0.05
4,800	301.0	5.8	3.7	.007

* These data are for commercial materials of unknown processing histories. The material was recrystallized at 2000°F for 1 hr

CREEP-RUPTURE PROPERTIES OF MOLYBDENUM-BASE ALLOYS

Table 1.13.9 and 1.13.10 show the creep-rupture properties of five arc-cast molybdenum base alloys. Preliminary data on the 2.4 Ti alloy showed outstanding creep-rupture results; however, because of defective test material, additional data could not be obtained. This material was stressed by increments to 45,000 lb/sq in. at 1800°F and 55,000 lb/sq in. at 1600°F without causing failure.

PROPERTIES OF HIGH-PURITY, SINTERED WROUGHT MOLYBDENUM METAL

Some properties of high-purity, sintered, wrought molybdenum metal at temperatures up to 2400°F are shown in Tables 1.13.11 and 1.13.12.

MELTING AND CASTING

Because of the high melting point of molybdenum and its susceptibility to embrittlement by impurities, particularly when cast, a special method for melting and casting has been developed. In this method, melting and casting are carried on in a vacuum (25 to 100 μ pressure), and heat is supplied by an electric arc maintained between a vertical, consumable molybdenum electrode and a pool of liquid molybdenum. The latter is contained in a water-cooled cylinder which serves as the casting mold. The arc melts the lower end of the consumable electrode causing droplets of molybdenum to gradually fill the water-cooled copper mold. The consumable electrode is formed continuously by extruding powder through a die. The extruded electrode is electrically sintered after it emerges from

Table 1.13.9—Creep-rupture Properties of Recrystallized Arc-cast Molybdenum-base Alloys* in Vacuum

Alloy	Stress, lb/sq in.	Rupture time, hr	Elongation, %	Reduction of area, %	1-hr heat treatment before test, °F	Approximate creep rate, %/hr
Tested at 1600°F						
2.4 Ti	32,500	450	Time in test at various stresses; test discontinued after a total of 840 hr		3200	...
2.4 Ti	45,000	148				
2.4 Ti	55,000	242				
0.32 Cb	32,500	2.9	43.5	84.6	2200	...
.32 Cb	25,000	59.6	27.7	75.0	2200	0.33
.32 Cb	24,375	136.8	35.4	53.8	2200	.087
.85 V	42,000	0.4	43.1	82.1	2400	...
.85 V	32,500	19.5	40.0	77.2	2400	0.15
.04 Co	41,500	0.9	46.0	77.0	2200	...
.04 Co	32,500	13.7	32.8	81.7	2200	...
.67 V	40,000	0.15	44.7	82.1	2200	...
.67 V	32,500	5.0	41.8	84.6	2200	2.3
Tested at 1800°F						
2.4 Ti	25,000	455.0	Time in test at the various stresses; test failed in adapter threads after a total of 616.5 hr		3200	...
2.4 Ti	35,000	97.0				
2.4 Ti	45,000	64.5				
0.32 Cb	30,000	0.4	58.5	91.0	2200	...
.32 Cb	25,000	4.0	46.7	87.6	2200	8.0
.32 Cb	20,000	97.4	60.3	87.9	2200	0.26
.85 V	32,500	0.8	45.3	91.0	2400	...
.85 V	25,000	19.7	48.4	91.5	2400	1.2
.85 V	20,000	203.5	43.2	69.7	2400	0.087
.04 Co	32,500	1.1	56.9	90.3	2200	...
.04 Co	25,000	10.5	86.9	92.2	2200	2.8
.04 Co	20,000	159.6	72.2	83.1	2200	0.16
.67 V	25,000	2.2	47.7	91.2	2200	...
.67 V	20,000	15.5	39.2	75.4	2200	...
.67 V	15,000	161.6	41.5	83.2	2200	...
Tested at 2000°F						
0.32 Cb	20,000	2.4	70.8	91.0	2200	...
.32 Cb	15,000	36.7	73.7	92.2	2200	0.51
.32 Cb	12,500	174.8	46.6	80.7	2200	.10
.85 V	22,500	2.4	62.7	83.0	2400	...
.85 V	15,000	75.1	51.9	77.7	2400	0.16
.04 Co	22,500	1.6	52.9	84.3	2200	...
.04 Co	16,000	55.5	56.9	86.4	2200	0.34
.67 V	22,500	0.6	61.8	86.5	2200	1.6
.67 V	15,000	21.2	70.6	87.8	2200	0.48

* All the ingots were cast in a 4-in. mold, turned to diameters ranging from $3\frac{1}{2}$ to $3\frac{3}{4}$ in., cut into two sections, the ends were noded and then forged, at 2600°F, to approximately $2\frac{1}{4}$ -in. octagons. These shapes were then rolled at a temperature of 2200°F to $\frac{1}{2}$ -in. round bars. The number of rolling passes for each billet varied between 20 and 29. The specimens machined from the $\frac{1}{2}$ -in. rounds had a gauged section $1\frac{1}{4}$ in. long and of $\frac{1}{4}$ -in. diameter for the recrystallized materials and $\frac{1}{8}$ -in. diameter for the stress-relieved materials

Table 1.13.10—Creep-rupture Data on Arc-cast Molybdenum-base Alloys in Stress-relieved Condition*

Alloy	Stress, lb/sq in.	Rupture time, hr	Elongation %	Reduction of area, %	Stress- relieving treatment before test, °F	Condition of specimen after test†	Creep rate, %/hr
1600°F							
0.32 Cb	75,000	0.2	12.3	74.4	1800
.32 Cb	65,000	13.3	13.2	74.4	1800	SR	0.04
.32 Cb	50,000	958.5	1.6	...	1800002
.85 V	75,000	1.3	10.9	74.4	1800
.85 V	60,000	6.1	9.5	59.2	1800	...	0.25
.85 V	50,000	288.9	11.2	45.4	1800	SR	...
.04 Co	70,000	1.3	18.4	68.6	1800
.04 Co	65,000	8.4	13.7	73.3	1800	...	0.12
.04 Co	53,000	319.6	16.6	75.0	1800	SR	.032
.67 V	60,000	2.8	13.6	74.6	1800
.67 V	50,000	68.4	14.8	78.1	1800
.67 V	46,000	131.4	22.1	79.5	1800	SR	0.024
1800°F							
0.32 Cb	55,000	2.8	16.1	77.2	1800	PR	0.08
.32 Cb	40,000	60.0	(Failed in adapter)	...	1800
.32 Cb	30,000	298.6	22.5	73.1	1800	PR	0.005
.85 V	70,000	0.1	12.2	67.6	1800	SR	...
.85 V	50,000	20.5	16.2	68.4	1800	SR	0.14
.85 V	40,000	104.3	16.4	73.8	1800	SR	.004
.85 V	31,000	338.6	7.9	...	1800
.04 Co	50,000	1.7	6.6	73.2	1800	PR	...
.04 Co	40,000	39.8	15.0	72.2	1800	PR	...
.04 Co	32,500	110.6	13.5	79.5	1800	PR	...
.04 Co	22,500	139.5	44.9	80.6	1800	R	...
.67 V	45,000	1.4	20.3	75.0	1800	PR	1.5
.67 V	35,000	19.0	19.1	81.6	1800	PR	0.19
.67 V	27,500	111.8	21.6	81.6	1800	PR	.028
.67 V	21,000	169.5	24.8	83.5	1800	R	...
2000°F							
0.32 Cb	15,000	37.7	38.6	70.6	None	R	...
.85 V	15,000	150.8	12.3	54.9	None
.04 Co	15,000	76.3	20.6	39.6	None	R	...
.67 V	29,300	1.1	23.5	79.1	None
.67 V	15,000	20.9	60.7	83.5	None	R	...

* All the ingots were cast in a 4-in. mold, turned to diameters ranging from 3½ to 3¼ in. and cut into two sections, the ends were nosed and then forged at 2600°F to approximately 2¼-in. octagons. These shapes were then rolled at a temperature of 2200°F to ¾-in. round bars. The number of rolling passes for each billet varied between 20 and 29. The specimens machined from the ¾-in. rounds had a gauged section 1¼ in. long and of ¼ in. in diameter for the recrystallized materials and ¾ in. in diameter for the stress-relieved materials

† SR-stress relieved; PR-partially recrystallized; R-recrystallized

Table 1.13.11—Typical Short-time Tensile Strength of High-purity, Sintered Wrought Molybdenum Bars*

Test temperature, °F	Ultimate tensile strength, lb/sq in.	Elongation in test section, %
Room	91,400	23.0
1800	30,500	18.7
2000	27,700	21.0
2200	21,400	29.1
2400	18,500	27.5

* Tests gauge section was $\frac{1}{4}$ in. in diameter and $\frac{1}{2}$ in. long

Table 1.13.12—Typical Short-time Strength of $\frac{1}{4}$ -in. High-purity, Sintered, Rolled Molybdenum Plate*

Direction	Test temperature, °F	Ultimate tensile strength, lb/sq in.	Elongation in test section, %
Longitudinal	Room	87,300	2.4
	1800	35,190	30.1
	2000	32,400	23.1
	2200	28,700	17.8
	2400	22,300	10.5
Transverse	Room	97,900	1.8
	1800	40,650	14.5
	2000	35,000	13.4
	2200	27,000	11.8
	2400	24,310	...

* Test section was $\frac{1}{2}$ in. long and $\frac{1}{4}$ in. in diameter

the die and is thus given sufficient strength to support its own weight. Continuous solidification of the ingot occurs at the same rate as melting, and because of the high thermal gradient induced by water cooling of the mold, the shrink hole or pipe is relatively small and concentrated near the top of the ingot. Only ingots have been cast so far.

FORMING AND FABRICATION

Since the ductile-to-brittle transition in molybdenum is often above room temperature, forming operations such as shearing, bending, crimping, drawing, upsetting, and spinning should be performed at elevated temperatures to minimize the occurrence of brittle cracks, particularly for heavier stock. For those forming operations in which the applied stresses induce high biaxial tensile stresses, the rates of deformation should not be high. Many forming operations that result in cracks when conducted at room temperature are entirely feasible and readily performed at temperatures of about 400°F.

EXTRUSION

The forming of molybdenum by extrusion of arc-cast ingots can be done directly by the Ugine-Sejournet Process. This is a recent development so that the sizes obtainable are not yet known.

Worked powder-metallurgy billets have been extruded using standard extrusion techniques to produce tubes of $\frac{1}{8}$ to 1 in. OD.

DRAWING

Deep drawing of molybdenum with wall reductions of up to 22 percent has been done. Drawn molybdenum seamless tubing is now available in lengths up to 48 inches for $\frac{1}{8}$ in. OD (11-mil wall) and in lengths up to 12 in. for $\frac{1}{2}$ in. in OD (90-mil wall).

In drawing molybdenum the number of draws should be held to a minimum to avoid the possibility of cracking, and if possible, the part should be designed to be drawn in one operation. Materials with low coefficients of friction, such as aluminum bronze, are recommended for dies. Steel dies, well lubricated with light oil, have also been used.

Wire drawing of molybdenum is accomplished in heated dies using standard techniques.

SPINNING

Spinning of molybdenum can be accomplished conventionally provided the sheet is maintained at about 400°F. Aluminum bronze tools or other materials of low coefficients of friction are employed.

ROLLING AND FORGING

Powder-metallurgy sintered ingots are rolled directly; arc-melted ingots are initially forged (at about 2400°F) to break down the cast structure and then rolled. Bar and rod are rolled in standard tool steel passes at 2100°F.

SWAGING

Molybdenum is readily swaged using conventional practice. (See also the following section on powder-metallurgy techniques.)

APPLICATION OF POWDER-METALLURGY TECHNIQUES TO MOLYBDENUM

The powder-metallurgy method was first applied successfully to prepare ductile molybdenum wire by Fink in 1910. The process has since been improved in detail and today each manufacturer introduces variations in procedure which produce minor variations in mechanical properties.

The process starts with powder of 99.97 percent purity, generally of 2 to 3 μ particle size, which has been reduced from molybdic oxide or ammonium molybdate with hydrogen. The powder is die pressed into bars, about $1\frac{1}{2}$ in. square and 24 to 30 in. long, at 30,000 lb/sq in. The relatively weak pressed bars are sintered by electrical self-resistance in hydrogen at 3600°F. The current used is usually 5 to 15 percent below that needed to melt the compacted bars. The more dense and stronger sintered bars are then hot swaged into rod or rolled to sheet. Temperatures for initial swaging and rolling (between 2100° and 2300°F) are lowered gradually as working proceeds, fine wire being drawn at slightly above room temperature.

For more massive molybdenum, pressing of the powder is done hydrostatically.

MACHINING

Molybdenum can be shaped, sawed, turned, reamed, milled, drilled, and bored. It machines with a crumbling chip. Tungsten carbide tools are recommended, although it is possible to use high-speed steel tools. The best machining properties occur with worked molybdenum when a uniform fine fibrous structure exists. The depth of cut should always be greater than 0.005 in. to minimize tool wear. To prevent chipping, the tools must be very rigidly supported. Tool angles and rakes similar to those used for cast iron are satisfactory.

MILLING AND TURNING

For milling, carbide-tipped cutters have been found to be much superior to high-speed tools. Sulfur-base cutting-oil lubricants have proved satisfactory for turning and milling and are recommended for drilling, tapping, or threading. High-speed steel and carbide drills at speeds of 30 to 35 ft/min and a feed of 0.003 in. are recommended. Rethreading or retapping should be avoided to prevent chipping.

For grinding molybdenum, aluminum oxide silica-bonded wheels are used. Wheel speeds of 6,500 ft/min should be used with a maximum depth of grind of 0.0002 in. Grinding should always be performed with plenty of coolant.

Highly polished surfaces similar to the best chromium plate can be obtained by using standard buffing wheels.

Sintered bars, unworked, are machined slightly more easily than worked molybdenum.

Molybdenum can be roll-threaded by heating it and the die to 325°F.

PUNCHING, SHEARING, AND BLANKING

Punching, shearing, and blanking should never be done with the metal in a chilled condition. Sheet thicker than 0.020 in. should be warmed slightly, the temperature increasing with thickness. It is good practice to keep the dies warm by using some device such as an infrared lamp.

JOINING

Molybdenum has been joined successfully by spot welding, arc welding, soldering, and brazing. That part of the parent metal which has exceeded about 2500°F during welding may, when later tested at room temperature, be brittle but if tested above 400°F is usually ductile.

ARC WELDING

Arc welds are made with either argon or helium gas shields and a tungsten electrode.

RESISTANCE WELDING

Molybdenum can be resistance welded. The preferred method is to stamp or roll a series of serrations or dimples in one of the sheets to be joined, thus providing a number of projections at which welding will be localized. The resultant weld structure is somewhat brittle at room temperature.

Spot welds of fairly satisfactory quality can be made if the surfaces of both sheets to be joined are etched. Any molybdenum sheet to be brazed or welded should be thoroughly cleaned of grease and oxide immediately before joining.

Only welding equipment with precise controls should be used, since excess heating will result in extremely brittle welds. Individual control values and timing are best determined by experiment. Electrodes should be kept clean and well dressed.

ETCHING FOR SURFACE PREPARATION

Etching, in preparation for resistance welding or brazing with tantalum foil,³ is accomplished by immersing the molybdenum sheet for 10 sec at 194°F in the following solution:

Sulfuric acid (concentrated)	5 gal
Chromic acid	0.825 lb
Hydrofluoric acid	1 qt
Nitric acid (concentrated)	$\frac{1}{10}$ qt

The sheet should then be immersed in chromic acid cleaning solution (35 cm³ of saturated sodium chromate solution in 1 liter of concentrated sulfuric acid) until the blue oxide disappears.

Some difficulties may be experienced because of electrode contamination of external sheet surfaces and pickup of the external surface on the electrode. These may cause low-strength joints.

BRAZING

Brazing operations for relatively thin sheet can be done in a spot or seam welder using copper or silver solder as the brazing medium. If all parts are well cleaned, no flux is necessary. Copper alloy electrodes can be used in the welding machine, but tungsten-faced electrodes are better.

Nickel foil (or nickel powder) has also been found satisfactory as a brazing material.

For applications where temperatures beyond the melting points of copper or silver solder are encountered, tantalum foil of approximately 0.001-in. thickness is an excellent brazing medium. Resistance "brazing" must be used when tantalum foil is the medium. The tantalum foil is placed in the interface between the two molybdenum surfaces to be joined and the assembly placed between the electrodes of a resistance welding machine. Sufficient current is passed to melt the tantalum foil, but under these conditions the molybdenum does not melt or melts only imperceptibly even though it has a lower melting point than tantalum, since the molybdenum pieces are more massive and better cooled and since most of the heat is generated at the two interfaces. The whole operation is done under water which prevents oxidation of tantalum and cools the molybdenum. In service the tantalum diffuses into the molybdenum and practically disappears. This method is used in the electronic tube industry. Brazing should be done under water to prevent oxidation of the tantalum foil.

Heavier sections of molybdenum can be brazed in hydrogen atmosphere furnaces without the use of a flux. Experimental copper or silver solder brazes can be made with a torch, but a flux must be used, and the results are dependent largely upon the experience and skill of the operator.

HEAT TREATMENT

All heating of molybdenum to temperatures above about 800°F (except for brief periods, such as for machining) should be done in reducing or neutral atmospheres, for example, in hydrogen or noble gas.

Heat treating for stress relief is done at 1850°F for 3 min.

Annealing temperatures for maximum ductility are from 1600° to 2100°F with time varied to obtain a small amount of recrystallization.

Annealing at temperatures above 2200°F is to be avoided since this usually results in a completely recrystallized structure of equiaxed grains often accompanied with brittleness at room temperature.

CORROSION BEHAVIOR

Molybdenum is characterized by the formation of soluble alkali molybdates and resistance to hydrofluoric and hydrochloric acids. Molybdenum is practically inert to cold solutions of sodium and potassium hydroxide, is attacked slowly by molten alkalis or sodium carbonate in the presence of air, but in the presence of oxidizing agents such as KNO_3 , KClO_3 , or PbO_2 rapid solution occurs.

ATMOSPHERIC

Molybdenum is stable in air at room temperature, although a polished surface becomes tarnished after several days' exposure.

Since it is difficult to nitride molybdenum in 1 atmosphere of nitrogen at temperatures up to 2700°F, it is presumed that the atmospheric effects are due to oxygen.

Oxidation occurs at elevated temperatures beginning at 1382°F. Above 1100°F the rate of evaporation of oxide, MoO_3 , begins to be appreciable, and at 1800°F in air, the surface is disappearing at the rate of 0.02 to 0.05 in./hr.

WATER

In the form of powder, molybdenum is oxidized in tap water and distilled water, but in compact form it is not attacked by hot and cold water. It reacts with water vapor at 1300°F.

LIQUID METALS

Information on the resistance to attack by liquid metals at 570° and 1110°F is given in Table 1.13.13.

Molybdenum has good resistance to molten lead and bismuth at 1800°F and good resistance to these metals under stress at 1500°F.

Molybdenum is attacked severely by gallium at 930°F showing deep penetration after 2 weeks.

Tests of a preliminary nature with molybdenum in contact with UO_2 and BeO for 100 hr at 2010°F showed no reaction.

In preliminary screening tests, molybdenum in contact with molten lead gained in weight, and a film, not identified, was found to form.

In compatibility tests at 1830°F for 40 hr in liquid sodium, no mass transfer was found between molybdenum and type 316 stainless steel.

Tests performed by immersing molybdenum in molten uranium-aluminum alloy (2 atom % U by weight) for 4 hr at 1830°F indicate that molybdenum cannot contain this uranium-bearing coolant at 1830°F.

PROTECTIVE TECHNIQUES

Protective techniques have all been directed toward preventing oxidation at temperatures above 1600°F. The most successful methods are to clad with Inconel or coat with molybdenum disilicide. The Fansteel Metallurgical Corporation is able to supply rod, wire, sheet, and tubing with coatings of molybdenum disilicide.

Table 1.13.13—Resistance of Molybdenum to Attack by Various Liquid Metals

(Liquid-Metals Handbook, edited by R. N. Lyon, Department of the Navy and U. S. Atomic Energy Commission, NAVEXOS P-733, June 1, 1950)

Liquid metal	Melting point, °F	Resistance of molybdenum*	
		570°F	1110°F
Hg	-37.97	Good	Good
Na, K, or Na-K	9.4 to 207.9	Good	Good†
Ga	85.6	Good	Poor
Bi-Pb-Sn	206.6	Unknown	Unknown
Sn	449.4	Unknown	Unknown
Bi-Pb	257	Unknown	Unknown‡
Bi	520.3	Good	Good§
Pb	621.3	Good (621.3)	Good¶
In	313.5	Unknown	Unknown
Li	367 ± 9	Good	Unknown
Tl	572	Unknown	Unknown
Cd	609.6	Unknown	Unknown
Zn	787	Unknown	Unknown
Sb	1166.9		Unknown
Mg	1202		Good (651)
Al	1220		Unknown

* Good—consider for long-time use; poor—no structural possibilities; unknown—no data for these temperatures

† Fair at 1830°F after 400 hr; intergranular attack to 1 mil depth after 100 hr at 2730°F in sodium vapor

‡ After 29 hr at 2000°F, 29 ppm of molybdenum was detected in the Bi-Pb eutectic

§ No appreciable attack after 160 hr at 1800°F; after 22 hr at 2000°F, 90 to 240 ppm of molybdenum was detected in the bismuth

¶ No appreciable attack at 1800°F in 250 hr

Other methods, such as ceramic coatings, electroplatings, and aluminum dip coatings, are being studied, but at this writing less success has been achieved than with cladding or siliconizing.

METALLOGRAPHY

Generally, two methods of preparing metallographic specimens have been used successfully: mechanical polishing and electrolytic polishing.¹ The choice between the two methods for any particular sample of molybdenum is sometimes difficult, and in some cases a combination of mechanical polishing and electrolytic polishing has given the desired result.

POLISHING TECHNIQUES

The specimen is rough ground to remove the cold-working effect caused by sectioning. Finer grinding can then be carried out by hand on metallographic papers. A still finer grind may be obtained using 600-grit carborundum paste on a canvas cloth. When working with molybdenum containing hard inclusions, the carborundum-canvas grinding technique has proved helpful in keeping relief of the inclusions to a minimum. The grinding operation is the same for both mechanical and electrolytic polishing.

¹References appear at end of chapter.

ELECTROLYTIC POLISHING

An electrolyte consisting of 175 ml of methyl alcohol and 25 ml of concentrated H_2SO_4 is recommended by Coons² for use on both arc-cast and sintered molybdenum as well as most of the molybdenum-base alloys. The specimen to be polished is the anode and is immersed in the electrolyte. Either stainless steel or platinum is used as the cathode. The electrolyte is maintained at room temperature during polishing. The potential is regulated between 12 and 18 and the current from 0.8 to 1.2 amp, for specimens with an area between $\frac{1}{2}$ and 1 square in. The polishing time varies between 30 and 90 sec depending on the particular material and on the type of inclusions that may be present. If the polishing operation is interrupted or if repolishing is desired, the specimen should be reground.

If the electrolyte becomes contaminated with water, a bluish oxide film is found on the surface of the sample. This oxide film may be removed by washing the sample in NH_4OH . The electrolyte should be replaced when the oxide of molybdenum begins to form.

MECHANICAL POLISHING

A more recent and less laborious technique than the familiar diamond-paste method described in the ASM Metals Handbook utilizes a rouge slurry. The time of polishing is short, and retaining some inclusions is accomplished more easily by this method than by the electrolytic method. The rouge-slurry method consists in using 15 gm of ferric oxide, 10 cm^3 of chromic acid (20 percent solution) and 100 cm^3 of water as the polishing solution. This is applied to a Forstman's cloth on a fast wheel (1750 rpm). Etch polishing is usually necessary to remove all the disturbed metal. However, etching should be light in order to keep relief to a minimum. The etching solution used during the etch polish operation consists of 10 gm of $\text{K}_3\text{Fe}(\text{CN})_6$, 10 gm of KOH, and 100 cm^3 of water.

In some instances, the rouge-slurry method causes considerable relief which can easily be eliminated by a very short final polish using aluminum oxide (Linde "B") on Forstman's cloth.

ETCHANTS

Either immersion-type etching or electrolytic etching can be used successfully on molybdenum. For pure molybdenum and for alloys the following solution has been found to be quite satisfactory; 10 gm of $\text{K}_3\text{Fe}(\text{CN})_6$, 10 gm of KOH, and 100 cm^3 of water. All etching should be performed by dipping or otherwise immersing the specimen since swabbing with cotton usually results in a finely scratched surface. The time of etching varies from 10 sec to 1 min depending on the degree of etching desired.

Another immersion-type etch reported by Coons, which is reported to be particularly well suited for etching molybdenum-base alloys, is as follows: 89 gm of NaOH, 25 gm of $\text{K}_3\text{Fe}(\text{CN})_6$, and 3800 ml of water. The actual etching solution consists of 20 to 30 ml of this solution added to 100 ml of water. The diluted solution must be fresh to be effective. The time of etching for this solution varies from 10 to 16 min.

FRAC TOGRAPHIC EXAMINATION

Another useful tool in the study of the structure and microconstituents in molybdenum has been the examination of grain surfaces following fracture. These examinations are now being made at all magnifications that can be obtained with the microscope.

The methods are simple and extremely fast and with a little experience, many of the microconstituents in molybdenum can be identified. A freshly made fracture which has not been exposed to the atmosphere or contaminated by handling after fracture should be examined. This method enables detection of extremely small quantities of impurities in molybdenum which cannot be detected by conventional metallographic techniques.

CONSTITUTIONAL DIAGRAMS

Only a few diagrams have been established for binary and ternary systems with molybdenum as one component, and many of these are incomplete. From what is now known about molybdenum alloys, a few summarizing statements can be made which may be helpful in predicting behavior in unknown systems. All the elements that are known to form solid solutions with molybdenum over an appreciable range of composition are transition elements. All the transition metals investigated thus far (except possibly manganese and the rare earths) form solid solutions. The Group I metals form neither solid solutions nor compounds with molybdenum.

The only molybdenum-rich alloy of commercial importance is ferromolybdenum (60 to 65 percent Mo) which is used to produce molybdenum steels and cast iron. Alloys of molybdenum and tungsten are obtainable on special order. The principal phase diagrams of molybdenum are readily available in other source books. The better known binary diagrams together with a source reference are given in Table 1.13.14.

Table 1.13.14—Principal Binary Constitutional Diagrams of Molybdenum

System	Reference
Molybdenum-nickel Molybdenum-tungsten Molybdenum-iron Molybdenum-chromium Molybdenum-carbon	"Metals Handbook," 1948 Edition, edited by T. Lyman, The American Society for Metals, Cleveland
Molybdenum-cobalt	
Molybdenum-beryllium Molybdenum-aluminum Molybdenum-silicon	
Molybdenum-titanium Molybdenum-uranium	
	M. Hansen, "Der Aufbau der Zweistofflegierungen," Springer-Verlag, Berlin, 1936
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CHAPTER 1.14

Nickel and Its Alloys

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REACTOR APPLICATION

Nickel and its alloys are useful in reactor engineering principally as materials of construction. The relatively high thermal-neutron-absorption cross section of nickel and its alloys limits their use to applications requiring special strength and corrosion resistance. Nickel-base alloys, in comparison with other corrosion resisting materials, are noted for high strength and are among the strongest materials known for service at high temperatures. Several have room-temperature mechanical properties equal to those of hardened steel. High-temperature, high-strength alloys of particular interest are Inconel "X," Nimonic "80," and Nimonic "90." Nickel-base alloys also have superior toughness and have moduli of elasticity at least the equal of steel.

Nickel and its alloys combine excellent corrosion resistance with good mechanical properties. Their corrosion resistance is especially good in the atmosphere, in liquid sodium, potassium, and sodium-potassium mixtures, and in caustic media of all kinds. In addition, within the nickel-alloy family are compositions especially resistant to the mineral acids and many halogen compounds.

Many nickel alloys are designed for special purposes. Compositions are available with special thermo-elastic properties, special thermal-expansion properties, and a variety of unusual magnetic properties. A detailed coverage of all nickel alloys is beyond the scope of this chapter, but data typical of some of the major alloy families are given. The reader is referred to extensive literature of the International Nickel Company and other producers for complete coverage of the several hundred known nickel alloys. Table 1.1.1 gives the nominal composition of various grades of nickel and some nickel alloys.

ABUNDANCE AND AVAILABILITY

Nickel is widely distributed in the earth's crust, particularly in the igneous rocks. It has been estimated that the average nickel content of the earth's crust is 0.019 percent, ten times its copper content. However, nickel is not often concentrated in nature in easily workable deposits in contrast to the many workable deposits of copper. Nevertheless, several important nickel-mineral deposits, containing substantial reserves of nickel, do exist in ore bodies now being worked or considered to be workable. The majority of these deposits are accessible to the free world.

The important nickel deposits, whether actual or potential ore bodies, are of two general types: (1) primary deposits in which the nickel-containing minerals are sulfides, arsenides, or, less commonly, silicates; and (2) secondary lateritic deposits which result from weathering of primary deposits and consist chiefly of complex silicates.

Table 1.14.1—Nominal Composition of Nickel and Some of Its Alloys

Material and form	Composition, %									
	C	Mn	Fe	Si	S	Cu	Al	Cr	Ni*	Other
Pure nickel, electrolytic	99.95	...
"A" Nickel, wrought	0.05	0.2	0.15	0.05	0.005	0.1	99.4	...
Nickel zirconium, wrought	.01	.30	.08	.11	.005	.02	99.02	0.27 Zr
Duranickel,† wrought	.17	.3	.35	.5	.005	.05	4.4	...	93.7	...
Monel, wrought	.15	1.0	1.4	.1	.010	30.0	67.0	...
"K" Monel,† wrought	.15	0.75	0.9	.5	.005	29.0	2.75	...	66.0	...
Inconel, wrought	.08	.25	7.0	.25	.007	0.2	...	15.0	77.0	...
Inconel "X,"† wrought	.04	.5	7.0	.4	.005	.05	0.9	15.0	73.0	1.0 Nb 2.5 Ti
Incoloy, wrought	.06	.80	Bal	.50	.01	.02	...	20.5	32.0	...
Illium "R," wrought	max	max		max	max	max				
Hastelloy "A," cast or wrought	.05	.3	6.0	.15	...	2.5	...	22	64.0	5 Mo
Hastelloy "A," cast or wrought	.12	3.0	19.0	1.0	1.0	Bal	21 Mo
Nimonic "80,"† wrought or cast	max	max		max				max		
	.10	1.0	5.0	1.0	1.2	20.0	Bal	2.25 Ti 2.0 Co (max)

* Nickel plus cobalt

† Age hardening

A distinction is made between actual ore bodies and potential ore bodies, because the winning of nickel is now in a state of technological flux. Until recent years, only the sulfide, arsenide, and very high grade silicate ores could be treated economically. The major free-world sources of nickel were the Sudbury district of Canada, the island of New Caledonia, the Union of South Africa, Norway, Greece, and Burma.

During World War II, a process was developed for extracting nickel from the low-grade laterite deposits of Cuba. Though considerable tonnages of nickel were obtained, the operation was uneconomical by peacetime standards. However, with changing economic conditions and technological improvements, the process is now expected to be competitive with the older established methods, and the Cuban enterprise has been reactivated as a peacetime venture. Should this operation prove successful, it will probably lead to additional economical processes for winning nickel from other low-grade laterite deposits now classified only as potential ore bodies. Such a deposit, now under active investigation, is located on Riddle Mountain, Oregon.

World production of nickel is about 170,000 metric tons. Of this, some 80 percent is produced by Canada, about 17 percent by the USSR, while the balance is supplied from New Caledonia, South Africa, Norway, and Greece.

EXTRACTION AND PURIFICATION

Several processes are used to extract nickel from its ores. The choice of process depends largely on the nature of the ore. Three commercial processes, two based on sulfide ores and one on silicate ores, are briefly as follows:

1. In extracting nickel from the sulfide ores of the Sudbury district, which also contain considerable copper, the ore is ground and classified by flotation. The products are a nickel-sulfide concentrate, containing some copper sulfide, and a copper sulfide concentrate. The nickel sulfide concentrate is roasted to oxidize the iron and remove some sulfur, then smelted to a matte in a reverberatory furnace, and the matte blown in a converter to eliminate more sulfur and most of the iron. The nickel and copper sulfides in the blown matte are separated by controlled cooling from the molten state. The nickel sulfide is leached and sintered, lowering the sulfur content to about 0.4 percent, then melted and cast into anodes which are refined electrolytically. The product is cathode nickel containing about 99.9 percent nickel plus cobalt. The range of the cobalt content is usually 0.1 to 0.3 percent. The impurities, usually totalling less than 0.1 percent, may be copper, iron, carbon, sulfur, and silicon.

2. In the Mond process, crushed nickel sulfide matte is roasted in two stages, reducing the sulfur content to about 1 percent. The product is then reduced to metal with water gas after which it is treated with carbon monoxide to form gaseous nickel carbonyl. The nickel carbonyl gas is passed over pure nickel pellets at 355°F, whereupon the gas decomposes and deposits nickel on the pellets. The nickel pellets resulting from the Mond process contain 99.9 percent or more nickel with small amounts of iron and traces of sulfur and carbon.

3. The nickel silicate ore of New Caledonia is dried, briquetted with gypsum and lime, and smelted in a blast furnace. The product, a double sulfide of iron and nickel, is blown in a converter to remove the iron. The resulting nickel sulfide is double roasted to nickel oxide with a sulfur content of 0.01 percent or less. The nickel oxide, in turn, is ground and agglomerated into cubes or small cylinders with an organic binder; these are heated with charcoal. The resulting cubes or rondels of nickel contain about 99.0 to 99.5 percent nickel plus cobalt.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants of nickel and some of its alloys are given in Table 1.14.2. Table 1.14.3 shows the variation of thermal conductivity with temperature for nickel and some of its alloys.

THERMAL-NEUTRON-ABSORPTION CROSS SECTION

The thermal-neutron-absorption cross section of nickel is 4.5 ± 0.2 barns/atom. The cross section of nickel alloys can be calculated on the method-of-mixtures basis.

CRYSTALLOGRAPHY

The crystal form of nickel is face-centered cubic. Although a close-packed hexagonal structure has been reported for some nickel films, nickel is not considered to have allotropic forms. The matrices of the commercial nickel alloys are face-centered cubic in structure. The lattice constant, a , of high-purity nickel is 3.5238 Å, while the closest approach of atoms is 2.491 Å. For wrought Monel, $a = 3.5481$ Å. The theoretical crystal (i.e., X-ray) density of nickel is 8.906 g/cm³.

HEALTH HAZARDS, HANDLING, AND STORAGE

Nickel and the common commercial alloys of nickel, such as those discussed in this section, are nontoxic in the solid state. No special precautions are required in handling or storing nickel and its alloys. They are not affected adversely by exposure to extremely low temperatures. They do not rust and are resistant to atmospheric corrosion and, hence, do not need special protection from the weather.

Table 1.14.3—The Variation of Thermal Conductivity with Temperature for Nickel and Some Nickel Alloys*

Temp., °C	Thermal conductivity, cal/(sec)(cm)(°C)			
	"A" Nickel	Monel	Inconel	Inconel "X"
100	0.155	0.060	0.039	0.038
200	.139	.065	.041	.043
300	.122	.070	.043	.048
340
400	.112	.074	.045	.054
500	.123	.079	.048	.060
525	.127
600	.136	.084	.050	.065
700089	.052	.073
800094	.054	.081

* Condition: annealed, with exception of Inconel "X" which was fully heat treated

MECHANICAL PROPERTIES

TENSILE PROPERTIES AND HARDNESS

The tensile properties, moduli of elasticity, and hardnesses of nickel and some nickel alloys are given in Table 1.14.4. Both room-temperature and elevated-temperature properties are presented in this table.

IMPACT STRENGTH

The impact strength or notch toughness of nickel and nickel alloys is shown in Table 1.14.5.

SHEAR STRENGTH

The shear strength of "A" Nickel, Monel, "K" Monel, and Inconel in several conditions is given in Table 1.14.6.

CREEP AND RUPTURE STRENGTH

The creep properties of "A" Nickel, Monel, "K" Monel, Inconel, Inconel "X", and Incolloy are given in Table 1.14.7. The data give the secondary creep rate expressed as the maximum stress which will produce a secondary creep rate of 0.01 and 0.10 percent in 1000 hr. Creep data on nickel zirconium are given in Table 1.14.8. Table 1.14.9 gives the rupture strength of Inconel and Incolloy.

TORSIONAL PROPERTIES

Johnson's apparent elastic limit and the angle of twist for "A" Nickel, Monel, "K" Monel, and Inconel are given in Table 1.14.10.

Table 1.14.4 — Tensile Properties and Hardnesses of Nickel and Some Nickel Alloys

Material and condition	Temp., °F	Proportional limit, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Modulus of elasticity, 10 ⁶ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Brinell hardness
Pure nickel, annealed	Room	4.5	8.5	46.0	30	30	...	85
"A" Nickel								
hot rolled	Room	18.0	21.0	63.0	30	51	...	107
	600	...	19.5	61.5	29	54
	1200	...	10.0	21.5	18	76
Duranickel								
hot rolled	Room	...	50.0	105.0	...	35	...	180
hot rolled and age hardened	Room	...	130.0	170.0	30	15	...	320
Monel								
hot rolled	Room	...	30.0	79.0	26	46	...	150
	600	...	21.5	75.0	25	50
	1200	...	14.5	36.5	13	36
	1800	...	2.5	5.0	5	60
annealed	Room	...	35.0	75.0	26	40	...	125
cold drawn	Room	...	80.0	100.0	26	25	...	160
"K" Monel								
hot rolled	Room	...	49.0	97.0	26	44	...	241
	800	...	39.0	87.0	...	29.5	...	207
	1200	...	44.0	63.0	...	2.5
	1600	15.0	...	53
hot rolled and aged	Room	...	111.0	160.0	...	23.5	...	331
	800	...	105.0	124.0	...	8.5	...	303
	1200	...	80.0	80.0	...	1.5
	1600	21.0	...	23
cold drawn	Room	...	85.0	115.0	...	25	...	210
cold drawn, aged	Room	...	115.0	155.0	...	20	...	260
Inconel								
hot rolled	Room	...	36.5	90.5	31	47	...	180
	600	...	31.0	90.5	29.5	46
	1200	...	26.5	65.0	20	39
	1800	...	4.0	7.5	11.5	118
annealed	Room	...	35.0	85.0	31	45	...	150
cold drawn	Room	...	90.0	115.0	...	20	...	260
Inconel "X"								
hot rolled and aged at 1300°F	Room	...	132.0	184.0	...	24	37	350
	600	...	125.0	176.0	...	26	40	...
	1200	...	100.0	142.0	...	12	17	...
Incoloy								76 Rock- well B
hot rolled	Room	...	45.0	90.0	...	40
Illium "R"								
solution annealed	Room	32.0	50.0	113.0	31	46	53	180
full hard	Room	67.0	128.0	142.0	28	11	44	300
Hastelloy "A"								
annealed	Room	...	44.0	110.0	27	50	45	175
	900	92.0	...	50
	1800	32.0	...	16
Nimonic "80"								
solution treated	390	...	91.0	146.0	...	45	26	...
at 1975°F for 8 hr - air cooled - aged 16 hr	570	...	91.0	143.0	...	44	43	...
	930	...	82.0	129.0	...	45	43	...
at 1290°F, air cooled	1470	...	63.0	71.0	...	8	10	...
Nickel-zirconium								
annealed	Room	...	37.0	72.0	...	46	82	...
cold drawn	Room	...	80.0	96.0	...	28

Table 1.14.5—Notched-bar Impact Strength of Nickel and Some Nickel Alloys

Material and condition	Temp., °F	Impact strength, ft-lb	
		Isod	Charpy
"A" Nickel			
hot rolled	Room	120	197
cold drawn	Room	120	195
annealed	Room	120	222
Duranickel			
hot rolled	Room	120+	240+
hot rolled, aged	Room	25	36
cold drawn	Room	120+	190
cold drawn, aged	Room	25	41
Monel			
hot rolled	Room	110	220
cold drawn	Room	95	150
annealed	Room	105	215
forged	Room	95	200
"K" Monel			
hot rolled	Room	120+	170
hot rolled, aged	Room	40	61
cold drawn	Room	56	71
cold drawn, aged	Room	26	42
Inconel			
annealed	Room	...	180
	1000	...	180
	1400	...	154
cold drawn	Room	...	114
	1000	...	86
	1400	...	163
Inconel "X"			
solution annealed	75	...	37
	1000	...	49
	1000	...	113
hot rolled	75	...	36
	1000	...	40
	1000	...	62
Illium "R"			
annealed	75	...	42
annealed	1000	...	35
Eastelloy "A"			
annealed	Room	40	...

Table 1.14.6—Shear Strength of Nickel and Some Nickel Alloys

Material and condition*	Shear strength,† lb/sq in.	Rockwell hardness
"A" Nickel		
soft	52,000	46R _B
half hard	58,000	90R _B
full hard	75,000	100R _B
Monel		
soft	49,000	61R _B
half hard	55,000	89R _B
hard	65,000	100R _B
"K" Monel		
soft	65,000	1R _C
soft, age hardened	96,500	29R _C
half hard	71,000	25R _C
half hard, age hardened	98,500	31R _C
full hard	89,500	33R _C
full hard, age hardened	98,500	37R _C
Inconel		
soft	61,000	71R _B
half hard	66,000	98R _B
full hard	84,500	31R _C

* Soft, half hard, and full hard are temper designations

† Strength in double shear; specimens 0.050 in. × 0.25 in.

Table 1.14.7—Creep Strength of Nickel and Some Nickel Alloys

Material and condition	Temp., °F	Stress, lb/sq in., to produce a secondary creep rate/1000 hr of	
		0.01%	0.10%
"A" Nickel hot rolled	600	23,500	52,000
	700	8,800	19,000
	800	3,700	7,800
	900	...	4,200
	1000	...	3,100
	1100	...	2,600
Monel hot rolled	700	30,000	40,000
	800	14,500	25,500
	900	4,000	13,500
	1000	...	3,000
cold drawn, annealed	750	20,000	30,000
	800	15,000	24,000
	900	8,000	16,000
	1000	3,500	9,500
"K" Monel cold drawn, age hardened	750	67,000	...
	800	48,000	...
	900	25,000	45,000
	1000	8,500	21,000
	1100	...	9,500
Inconel hot rolled	800	46,000	57,000
	900	30,000	42,000
	1000	14,500	25,000
	1100	7,200	12,000
	1300	4,000	6,400
	1500	680	1,400
Inconel "X" solution treated and double aged	1100	75,000	...
	1200	54,000	...
	1350	30,000	...
	1500	14,000	...
	1600	7,000	...
Illium "R" solution treated	1200	...	15,000
	1500	...	5,200

Table 1.14.8—Creep Data* on Nickel—Zirconium

Stress, lb/sq in.	Maximum creep rate, %/hr	Total extension, %	Test duration, hr
15,000	0.000020	0.087	1632
20,000	.00058	.167	2016

* Specimens tested in air at 950°F after annealing 2 hr at 1550°F

Table 1.14.9—The Rupture Strength of Inconel and Incoloy at Various Temperatures

Material and condition	Test temp., °F	Stress, lb/sq in. to produce rupture in:		
		1,000 hr	10,000 hr	100,000 hr
Inconel	1000	34,000	23,000	16,000
Cold drawn	1200	14,500	9,400	6,000
and annealed	1400	5,600	3,800	2,400
	1600	3,000	1,900	1,200
	1800	1,800	1,150	730
	2000	920	620	400
Inconel	1350	9,200	6,400	4,400
Hot rolled	1600	3,500	2,200	1,500
and annealed	1600	1,800	1,150	730
2 hr at 1650°F	2000	920	620	400
Incoloy	1400	8,700	6,000	4,200
Coarse grained- annealed	1600	3,800	2,200	1,300
	1800	1,700	1,100	670
	2000	850	540	...

Table 1.14.10—Torsional Properties of Nickel and Some Nickel Alloys

Material and condition	Proportional limit, lb/sq in.	Johnson's apparent elastic limit, lb/sq in.	Angle of twist, deg/in.
"A" Nickel			
cold drawn	48,000	63,000	341
Monel			
hot rolled	25,000	...	340
cold drawn	51,000	56,000	...
"K" Monel			
hot rolled	27,000	29,000	620
hot rolled, age hardened	57,000	67,000	104
cold drawn	48,000	55,000	360
cold drawn, age hardened	62,000	71,000	76
Inconel			
cold drawn	50,000	54,000	302

MELTING AND CASTING

Nickel and nickel alloys may be melted in electric-arc, induction, and oil- or gas-heated furnaces. Danger of contamination by sulfur limits the use of coke-heated pit melting. The preferred furnace linings are the neutral and basic types.

Since minor elements such as lead and sulfur have harmful effects on the mechanical and welding properties of nickel-base materials, extreme care should be exercised to prevent such contamination.

To avoid gassy heats, a thorough drying of the charge, furnace linings, and ladles is essential. This is of particular importance for production of nickel and nickel-chromium alloys.

RECOMMENDED MELTING PRACTICE

Nickel is melted under a thin, protective slag of limestone. Oxidation of the heat is accomplished by additions of nickel oxide made during or immediately after melt-down. Dissolved gases are then removed from the molten metal by adding a sufficient amount of carbon to cause a boil by reaction with the oxygen present and maintaining the boil until the gases are removed. The boil is killed by a small silicon addition after which charcoal is added to bring the carbon content up to the desired level. To flux any oxides present in the heat, manganese is added before tapping. When the heat has reached the tapping temperature, it is poured and deoxidized in the ladle using silicon and magnesium additions. The pouring temperature ranges between 2750° to 2900°F depending on the size of casting to be made and the kind of mold used.

For nickel-copper alloys, such as Monel, a straight melt-down is used when the charge is scrap of known origin. As in the melting of nickel, a thin, protective slag of limestone is employed. An adjusting addition of manganese is made using a silicon-manganese alloy. After reaching the desired tapping temperature, the heat is deoxidized in the ladle.

Production of Monel castings from electrolytic nickel and copper involves, first, charging the copper and sufficient charcoal to bring the carbon content to the desired level and then adding the nickel. Melting is done under a thin limestone slag. Excess charcoal is removed from the melt, and the silicon and manganese additions are made as described previously. The pouring temperature range is 2650° to 2850°F.

In the melting of nickel-chromium alloys, the chromium is charged on top of approximately half the nickel, the remainder of the nickel being charged after the chromium. Nickel or iron oxides are added in sufficient amounts to ensure an oxidized bath. The melt-down is made under a protective limestone slag to which cryolite has been added to ensure fluidity. After the dissolved gases are removed by the boil, silicon is added to kill the boil, and calcium silicon is dusted on the surface of the slag to maintain reducing conditions. The bath is cleaned and deoxidized with 0.10 percent magnesium added in the furnace when the tapping temperature of 2850° to 3100°F has been reached. Silicon and manganese are added in the ladle, together with a 0.05-percent-titanium addition if the nitrogen is to be fixed. The pouring temperature is varied between 2800° and 2950°F depending on the size of the casting and the type of mold used.

FORMING AND FABRICATION

HOT FORMING

The hot working and hot forming of nickel and nickel-base alloys requires closer control of working temperature and atmosphere than is needed for other nonferrous alloys and steels. Working of high-nickel alloys in a low-sulfur atmosphere at high temperatures is essential to prevent intergranular attack and embrittlement. The use of coal or coke

for heating is not recommended since the atmosphere produced will usually have a high sulfur content. Recommended fuels include low-sulfur city gas or fuel oil, natural gas, butane, and propane.

Although heating at high temperatures for prolonged periods is not considered detrimental to the Hastelloys, it should be avoided in other nickel alloys, the materials being heated only long enough to ensure temperature uniformity throughout. Since nickel-base materials do not carburize or scale readily, oxidation can be prevented by maintaining a reducing atmosphere containing approximately 2 percent excess carbon monoxide. Alternating from a reducing to an oxidizing furnace atmosphere must be avoided or severe intergranular attack and embrittlement will result.

The age-hardenable alloys (with the exception of the nickel-chromium varieties) should be water quenched after hot forming to prevent hardening during slow cooling. The other nickel alloys can be cooled in air after hot forming.

Because of the higher strength and greater toughness exhibited by nickel alloys at forging temperatures in comparison with steel, forging equipment must be heavier. Commonly employed forging techniques can be used, however, if correct heating methods are followed. The Hastelloys do not forge as readily as other high-nickel alloys because of the greater stiffness exhibited at high temperatures.

The hot-working and hot-forging temperatures for nickel and some nickel alloys are shown in Table 1.14.11. The Hastelloys must be forged above 1900°F to avoid cracking since these alloys are brittle when forged below this temperature.

Table 1.14.11—Hot-working Temperatures for Nickel and Some Nickel Alloys

Material	Temperature range, °F
"A" Nickel	2300 – 1600
Duranickel	2150 – 1850
Monel	2150 – 1600
"K" Monel	2150 – 1900
Inconel	2300 – 1850
Inconel "X"	2225 – 1900
Hastelloy "A"	2200 – 1950
Nimonic "80"	2100 – 1920

COLD FORMING

The majority of the nickel and nickel-base alloys can be cold worked. The cast alloys, however, because of their great brittleness and high hardness, cannot be cold worked satisfactorily.

In cold-working operations such as drawing, swaging, cupping, and bending, nickel, Monel, and Inconel behave similarly to mild steel except that more power is required to form them. "L" Nickel, being softer than regular nickel, does not work harden as rapidly; however, Duranickel which work hardens more rapidly than regular nickel can be cold worked heavily without fracturing because of its great ductility. "K" Monel hardens more rapidly with cold work than does Monel. Its ductility in the annealed condition permits severe deformation without cracking.

Since heavy cold working increases the hardness and tendency of the material to crack, intermediate anneals are required during severe cold-forming operations. It is important to keep work free from tool and die marks if heavy drafts are to be taken.

DEEP DRAWING

For nickel, Monel, and Inconel, special cold-rolled, deep-drawing quality sheet and strip are available. All bending and moderate drawing operations may be done on standard cold-rolled, soft-temper sheet. Soft-temper material most suited to deep drawing has a fine-to-medium grain; i.e., the grain size does not exceed 0.0025 in. average diameter.

Severe deep drawing of Hastelloys "A," "B," and "C," must be done in the hot-working range of these alloys (1900° to 2200°F). In general, after all hot- or cold-forming operations, the Hastelloys should be given a full or stabilizing anneal if they are to retain maximum corrosion resistance.

Die materials for deep drawing include hard alloy bronze, heat-treated nickel-chromium cast iron, and chromium-plated hardened alloy die steel. Chlorinated paraffins are recommended lubricants. Water-soluble and oil-soluble lubricants containing fillers, however, are also satisfactory.

SPINNING

In the annealed condition, nickel and nickel-base alloys, such as Monel and Inconel, have sufficient ductility for spinning operations. However, frequent annealing is required because of the work-hardening characteristics of the alloys. Long, powerful strokes should be used in laying down the work on the chucks. Reworking and crowding the metal are to be avoided, the spinning being stopped when the metal ceases to flow. Carrying the spinning operation too far will result in surface cracking of the metal.

Bar tools are usually made of highly polished, hard alloy bronze while roller and beading tools are hardened, chromium-plated tool steels. The lubricant used for spinning should be heavy bodied to enable it to withstand the high temperature and pressures developed during the operation. Yellow laundry soap is the most commonly employed, although beeswax and tallow are satisfactory. Since special spinning stock is available for most alloys, it should be specified when the intended use demands a spinning operation.

SHEARING

Shearing of nickel alloys requires from approximately 115 to 150 percent of the power needed for shearing mild steel of equal gauge.

PUNCHING

Material for punching should be soft to skin-hard temper. Satisfactory total punch and die clearance for nickel, Monel, and Inconel is usually considered as 3 to 6 percent of the thickness of the material to be punched. Close clearance between the punch and stripper plate is advisable. Usually from 15 to 20 percent more shear load is required than for mild steel of equal gauge.

POWDER METALLURGY

NICKEL

Dense products of pure nickel from powder are currently being produced on a limited scale. The principal use of these products has been in the high-vacuum field.

Sintered nickel is manufactured from three types of powders:

1. Carbonyl nickel powder (99.0 to 99.9 percent nickel)
2. Pulverized shot obtained from fusion of electrolytic nickel (99.0 to 99.9 percent nickel)
3. Reduced nickel powder (99.0 percent nickel).

NICKEL-IRON

Nickel-iron alloys are the only nickel-base alloys produced on a commercial scale by powder methods at the present time. Low expansion characteristics or high, controllable magnetic properties of certain alloys are utilized in the communications field in the production of radio-tuning cores.

NICKEL-COPPER

Monels are not easily reproduced by powder-metallurgy techniques to give the same high quality found in wrought alloys. Sintering must be carried out in a vacuum or in a dry hydrogen atmosphere, the temperature approaching the melting point of the alloy.

NICKEL-CHROMIUM

Nickel-chromium alloys include Nichrome and Nimonic "80." Sintering is carried out for 2 to 6 hr at 2370° to 2460°F in vacuum or in highly purified hydrogen. Intermediate hot working may be necessary.

NICKEL-CHROMIUM-IRON

Inconels are produced from powder in a manner similar to that employed for nickel-chromium alloys.

NICKEL-CHROMIUM-COBALT

Nimonic "90" can be produced by vacuum sintering compacts of the elemental powders at 2370° to 2460°F. The strength of the material produced is controlled by particle size, the sintered metal being comparable to the cast metal in strength if the size of the powder particles used does not exceed 10 microns.

NICKEL-MOLYBDENUM-IRON

Hastelloys can be produced from extremely fine, pure powders, the product being made by vacuum sintering at 2370° to 2460°F.

JOINING

Joining processes applicable to nickel and nickel-base alloys are shown in Table 1.14.12.

Table 1.14.12—Joining Processes Applicable to Nickel and Some Nickel Alloys

Material	Welding							Brazing		Soft solder
	Metal arc	Atomic- hydrogen arc	Inert-gas metal arc	Submerged arc*	Oxyacety- lene	Oxyacetylene pressure	Resistance	Silver	Copper	
"A" Nickel	x	...	x	x	x	x	x	x	x	x
Duranickel	x	...	x	...	x	...	x	x	x	x
Monel	x	x	x	x	x	x	x	x	x	x
"K" Monel	x	x	x	...	x	x	x	x	x	x
Inconel	x	x	x	x	x	x	x	x	x	x
Inconel "K"	x	...	x	x	x	x	x	x
Hastelloy "A"	x	...	x	x	x	...	x

* Extreme caution must be exercised with regard to flux purity

MACHINING

The high strength, ductility, and toughness of nickel-base alloys decrease their machinability. These alloys, however, are not difficult to machine when proper tools, feed, speed, and cutting compound are used. Two Monels, "R," containing high sulfur, and "KR" containing high carbon, are free-cutting grades and can be machined in automatic screw machines.

In general, slower cutting speeds and lighter cuts than those used for steels are recommended. From the standpoint of economy and desirability, a deep cut and light feed should be used in turning and boring. Cutting tools having sharp cutting edges with minimum relief are recommended. The work also should be flooded with lubricant.

For turning wrought alloys, roughing tools should have front and side relief angles of 6 to 8 degrees, and finishing tools, from 12 to 15 degrees. Side rake angles vary from 10 to 25 degrees depending on the alloy and type of cut. A nose radius of $\frac{1}{8}$ in. for rough cuts and $\frac{1}{16}$ in. for finish cuts is recommended.

HEAT TREATMENT

STRESS EQUALIZATION

Cold-worked and hot-worked nickel and nickel alloys may be given a thermal treatment at relatively low temperature to develop an optimum combination of strength and ductility, to promote stability of dimensions and shape, or to minimize distortion and warpage upon subsequent machining. Temperatures range from 525° to 650°F for "A" Nickel and Monel and from 650° to 900°F for Inconel and Inconel "X." Hot-worked materials require higher temperatures than cold-worked metal. The treatment dissipates local concentrations of stress in the material and effects what is called "partial recovery," but produces no microscopically detectable structural changes.

Stress equalization is usually applied to coil springs, wire forms, and flat-spring stampings.

Age-hardening high-nickel alloys generally require no stress-equalization treatment after fabrication as the hardening operation takes care of it effectively. However, if the article is subjected to cold work after age hardening, it is advisable to give it a stress-equalizing treatment as a final operation, especially when the intended use involves fatigue or high stresses.

STRESS-RELIEF

Nickel and high-nickel alloys (excluding Inconel "X") are sometimes given a thermal treatment in the range of 1000° to 1300°F to remove or reduce internal microstresses which exist in the metal as a result of cold working, machining, casting, or welding operations. The treatment is employed where full annealing is not required. Inconel "X" is stress relieved at 1600° to 1650°F for 24 hr followed by air cooling.

ANNEALING

As the term is used here, annealing is a heating and cooling operation intended to soften work-hardened metal. The softening is brought about by recrystallization, i.e., replacement of the distorted grain structure of the worked metal by a new, strain-free grain structure.

In annealing nickel and its alloys the following factors should be observed:

(1) Protection against embrittlement caused by sulfidation or alternate oxidation and reduction resulting from the use of an annealing atmosphere which fluctuates in composition.

(2) Protection against excessive oxidation.

(3) Control of temperature and time at temperature to avoid excessive grain growth.

Annealing may be effected by either the "open" or "box" process.

The following temperatures are suggested for open annealing cold-worked nickel and nickel alloys:

Material	Temperature, °F
"A" Nickel	1500 – 1700
Duranickel	1600 – 1800*
Monel	1600 – 1800
"K" Monel	1600 – 1800
Inconel	1800 – 1950
Inconel "X"	2075 – 2125†

* Quench in a solution of 2 volume-percent alcohol in water

† Solution anneal; to soften, heat to 1900° to 2000°F and quench

AGE-HARDENING

Duranickel, "K" Monel, "KR" Monel, "S" Monel, Inconel "X," and Nimonic "75," "80," and "90" are age-hardenable nickel alloys. Specific age-hardening procedures are described in Technical Bulletin 16 of the International Nickel Company. In general, material cold worked after solution annealing requires lower aging temperatures and a shorter time at temperature to develop maximum mechanical properties than material aged in the soft condition. For Inconel "X," the aging procedure varies with the temperature at which the material is to be used.

CORROSION

ATMOSPHERIC

Generally, nickel and nickel-base alloys are not attacked by indoor or outdoor atmospheres unless they are sulfurous in nature. Marine atmospheres may promote a slight attack, but rural and suburban atmospheres have little, if any, effect on the corrosion of these alloys.

LIQUID METALS

The corrosion behavior of nickel and nickel alloys by liquid metals is shown in Table 1.14.13. Good corrosion resistance is exhibited by nickel alloys in molten sodium, potassium, or a combination of the two. The nickel-chromium alloys show good resistance in molten lithium. The corrosion of Inconel in various low-melting alloys at 1500°F is given in Table 1.14.14.

MOLTEN HYDROXIDES

Nickel in fused sodium hydroxide under reducing conditions involving a temperature gradient has been observed to dissolve in the hot zone and reprecipitate in metallic form in the colder area. Under neutral or oxidizing conditions, the deposit is largely nonmetallic in nature.

Solution and deposition of nickel has not been noted at 1000°F but has been observed at 1250°F and increases in severity with increasing temperature. At 1500°F it is much too

Table 1.14.13—Corrosion of Nickel and Some Nickel Alloys by Liquid Metals
(Liquid-Metals Handbook, NAVEXOS P-733, June 1, 1950)

Metal and melting point, °F	Resistance* of nickel alloys at indicated temperatures, °F							
	Nickel		Hastelloy "A," "B," "C"		Inconel, Nichrome, Chromel		Monel and other Ni-Cu alloys	
	570	1110	570	1110	570	1110	570	1110
Cadmium, 610	V	P	V	V	V	V	V	V
Aluminum, 1220	V	P	V	V	V	P	V	P
		1220				1220		1220
Mercury, -38	P	P	V	V	V	P	P	P
Zinc, 787	V	P	V	V	V	P	V	P
Sodium, potassium, or sodium-potassium, 10 to 208	G	G	G	G	G	G	G	G
Gallium, 86	V	P	V	V	V	V	V	V
Antimony, 1167	V	P	V	V	V	P	V	P
		1167				1167		1167
Magnesium, 1202	V	P	V	V	V	V	V	V
		1202						
Bismuth-lead-tin, 206	V	V	V	V	V	V	V	V
Bismuth-lead, 257	P	P	V	P	V	P	P	P
Tin, 449	P	P	P	P	P	P	P	P
Bismuth, 520	P	P	V	V	V	V	V	V
Lead, 621	P	P	V	V	V	V	P	P
	621							
Indium, 313	P	P	V	V	V	V	P	V
Lithium, 367	V	P	V	V	G	V	P	P
Thallium, 572	P	P	V	V	V	V	P	V
	572							

* V = No data available

P = Poor, not to be considered for structural use

G = Good, considered for structural use: penetration less than 0.001 in./yr

Table 1.14.14—Static Corrosion of Inconel by Various Low-melting Alloys in 100 Hours at 1500°F
(ANPP Quarterly Progress Report, ORNL-1227, March 10, 1952)

Alloy composition, wt-%	Depth of metal affected, mils	Metallographic notes
43 tin - 57 bismuth	8	Five mils of uniform layer on surface with an underlying layer of voids 3 mils thick
60 bismuth - 40 cadmium	Complete penetration	Voids throughout entire specimen
38 lead - 62 tin	6	Erratic attack
68 tin - 32 cadmium	2	Uniform attack
82 lead - 18 cadmium	10	Intergranular attack
44 lead - 56 bismuth	4	Intergranular attack

severe to permit nickel to be used as a container for fused caustic.

The mechanism whereby nickel is dissolved in the hot zone and is reprecipitated in the colder area is not yet clear. It is known that addition agents such as sodium aluminate and sodium carbonate are effective in reducing the solution and deposition of nickel up to a temperature of about 1500°F.

The static corrosion of nickel and nickel-base alloys in various hydroxides at 1500°F has been investigated at Oak Ridge. In these tests, the hydroxide and test specimen were contained in an evacuated capsule of the material being tested. All tests were run for 100 hr at a constant temperature (no intentional temperature gradient as described above). Results are summarized in Table 1.14.15. The data show that there is less attack on nickel

Table 1.14.15—Static Corrosion of Nickel and Nickel-base Alloys by Various Hydroxides for 100 Hours at 1500°F

(ANPP Quarterly Progress Report, ORNL-1170, December 10, 1951)

Alloy*	Testing medium	Depth of metal affected, mils	Metallographic notes
"A" Nickel	Sr(OH) ₂	0.0	No evidence of attack
"A" Nickel	NaOH	0.0	Slightly attacked
"A" Nickel	LiOH	0.0	No evidence of attack
Duranickel	Ba(OH) ₂	6.0	Erratic attack
Duranickel	Sr(OH) ₂	1.5	0.002-in. layer of attacked zone
Duranickel	NaOH	20.0	Severely attacked
Monel	Ba(OH) ₂	0.0	No evidence of attack
Inconel	LiOH	4.0	0.006-in. oxide layer
Inconel "X"	Ba(OH) ₂	6.5	0.020-in. oxide layer
Inconel "X"	Sr(OH) ₂	3.0	0.007-in. oxide layer
Hastelloy "B"	Ba(OH) ₂	9.5	Heavy oxide formed
Hastelloy "B"	Sr(OH) ₂	9.0	Specimen heavily oxidized and embrittled

* Specimens tested in evacuated capsule of like material

under static conditions than with a dynamic system involving a temperature gradient.

A thermal convection loop constructed of Inconel was run with hot and cold leg temperatures of 1315° and 825°F, respectively, for 135 hr without deposition when dehydrated potassium hydroxide was used as the test medium. Purified hydrogen was the ambient atmosphere. Systematic studies at Oak Ridge on the corrosion of Inconel by KOH have revealed that attack is a function of temperature, time of exposure, and ambient atmosphere. Pitting-type corrosion is noted at temperatures above 1000°F and is more pronounced in air or in vacuo than in hydrogen.

The effect of addition agents is also being investigated by Oak Ridge. A 50-percent addition of NaCN to sodium hydroxide appeared to lessen somewhat the attack on Inconel. However, none of the additives tested to date appeared to reduce corrosion to an insignificant level.

The problem of metal transfer in molten hydroxides is now being actively investigated. While some results are encouraging, a satisfactory solution to the corrosion problem, which will permit the use of nickel or nickel alloys with molten hydroxides at temperatures above 1250°F, has not yet been found.

HF-H₂O AT ELEVATED TEMPERATURES

"A" Nickel, "D" Nickel, "L" Nickel, Monel, "S" Monel, Hastelloy "C," Inconel, Inconel "X," and "K" Monel were exposed to HF and HF-H₂O atmospheres in furnaces operating between 950° and 1050°F. After 6 months of testing, it was found that Inconel had the best corrosion resistance under these conditions. "D" Nickel, Monel, and "K" Monel, although not as corrosion resistant as Inconel, gave sufficiently desirable service that their use under these conditions may be warranted. The other alloys, because of embrittlement, nature of scale formed, or complete disintegration, were eliminated as being useful in HF-H₂O atmospheres at elevated temperatures.

PROTECTIVE TECHNIQUES

Nickel-, Inconel-, and Monel-clad steels are available commercially. They are used for the construction of large corrosion-resistant equipment, saving much in material cost, while at the same time providing corrosion protection comparable to that of the cladding metal.

The clad steels are produced by hot rolling, the cladding material tending to form a solid solution with the steel at the interface between the cladding and the steel base. Thus, under normal conditions of temperature change, pressure, vacuum, or mechanical shock, no separation of layers occurs. Fabrication involving shearing, bending, flanging, forming, and joining does not affect the bond when proper precautions are taken.

METALLOGRAPHY

Nickel-base alloys are prepared for macro- and microexamination according to standard methods. In general, for microexamination concentrated nitric acid is used to etch nickel-copper and nickel alloys, while aqua regia is the etchant for nickel-chromium and nickel-chromium-iron alloys. For microexamination of nickel alloys, Carpella's Reagent or cyanide persulfate are commonly employed etchants. It may be necessary in some cases to warm the reagent or the specimen to initiate the reaction.

CONSTITUTIONAL DIAGRAMS

The following constitutional diagrams are given in the **METALS HANDBOOK**, 1948 Edition:

- | | | |
|----------------------|----------------------------|-------------------------------|
| 1. Nickel-silver | 13. Nickel-molybdenum | 25. Nickel-copper-beryllium |
| 2. Nickel-aluminum | 14. Nickel-oxygen | 26. Nickel-carbon-iron |
| 3. Nickel-gold | 15. Nickel-platinum | 27. Nickel-chromium-iron |
| 4. Nickel-carbon | 16. Nickel-sulfur | 28. Nickel-copper-tin |
| 5. Nickel-niobium | 17. Nickel-silicon | 29. Nickel-copper-zinc |
| 6. Nickel-cadmium | 18. Nickel-tin | 30. Nickel-iron-molybdenum |
| 7. Nickel-cobalt | 19. Nickel-tantalum | 31. Nickel-iron-silicon |
| 8. Nickel-chromium | 20. Nickel-titanium | 32. Nickel-iron-titanium |
| 9. Nickel-copper | 21. Nickel-tungsten | 33. Nickel-iron-tungsten |
| 10. Nickel-iron | 22. Nickel-zinc | 34. Nickel-molybdenum-silicon |
| 11. Nickel-magnesium | 23. Nickel-aluminum-copper | |
| 12. Nickel-palladium | 24. Nickel-aluminum-iron | |

SPECIAL ALLOYS

In this chapter, major emphasis has been placed on nickel, as a metal, and on the more usual alloys of nickel, such as the systems nickel-chromium, nickel-chromium-iron, and nickel-molybdenum. There is, in addition, a large group of nickel alloys with very unusual physical properties which suit the alloys to a variety of important special applications. These alloys are based on the nickel-iron system. Alloys have been developed which have special elastic properties (Elinvar and Ni-Spar), special thermal-expansion properties (Invar, Nilvar, and Platinite), and special magnetic properties (Permalloy and Hypernik).

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CHAPTER 1.15

Plutonium and Its Alloys

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The direction toward which the metallurgy of a metal tends to be strongly developed, or neglected, is an inevitable consequence of the applications for which it proves to be either well adapted or poorly promising. Plutonium is no exception to this rule. For example, there are obvious reasons why plutonium and its alloys are not expected ever to possess importance as structural materials, and, accordingly, very few data regarding their strength and related properties have been ascertained.

In the present state of knowledge, only two general fields of application of plutonium and its alloys appear to have either actual or potential importance. These are weapon applications and reactor applications.

REACTOR APPLICATION

As a reactor component, its principal role has been that of a product of the reactor reactions, the outstanding example of this being its part in the operations of the Hanford reactors. In one exceptional instance, the Los Alamos Fast Reactor, plutonium at present serves as the fuel for the nuclear reaction. Although the chief consideration involved in the selection of plutonium for this reactor was probably that no other reactor used it as fuel, its uniquely high average yield of approximately three neutrons per Pu^{239} fission makes it particularly applicable to a breeding operation. The full benefit of the high neutron yield can be effectively realized, however, only if the bombarding neutrons that cause fission are "fast," i.e., have high energy. Hence, one of the reasons for designing and building the reactor at Los Alamos as a fast reactor was to ensure that the advantages inherent in the high neutron yield of plutonium would be available.

Because the characteristics of plutonium are exceptionally promising for power-breeder requirements, the importance of this element, both as fuel and as product, may soon transcend that of all other fissionable materials used in nuclear reactors.

ABUNDANCE AND AVAILABILITY

Although plutonium does occur in nature, the one part in 10^{11} that has been found in pitchblende suggests that the total "natural abundance" of plutonium is too minute ever to

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have practical significance for reactors. Thus plutonium may be regarded as purely a synthetic element. Its "synthetic abundance" is limited, however, to the natural abundance of U^{238} , the only isotope from which plutonium may be expected to be practically derived.

The availability of plutonium for reactor applications is of course subject to the demand for plutonium for weapon applications.

EXTRACTION AND PURIFICATION

Because plutonium is a synthetic element, the initial steps involved in winning the metal from its source materials are radically different from correspondingly early procedures, such as ore dressing, roasting, and leaching, in the extraction of naturally occurring metals. The reduction to metal and purification of this metal are, however, similar to those methods used for the ultimate reduction and refinement of a number of other metals.

Strictly speaking, the winning of plutonium (as a process following but separate from the metallurgical extraction of uranium) must be considered to begin with the fabrication of the uranium fuel elements for the reactor in which the plutonium is to be produced. A complete account of the extractive metallurgy of plutonium would contain (1) a description of fuel-element formation (2) discussions of loading the reactor, as well as its operation and unloading, and (3) descriptions of chemical separation processes that yield material for reduction to metal. All operations preceding such final purification and reduction have been carried out as a production routine since 1944 when operation of the first Hanford reactor was begun.

Although details of the extractive metallurgy of plutonium will not be presented here, it is to be expected that in the plutonium power-breeder plant, all steps of the breeding cycle, both internal and external to the reactor, and including the reduction of plutonium to metal, would be carried out as an integrated regenerative process complete at any one location.

PHYSICAL CONSTANTS

Only those physical constants of pure plutonium are listed in Table 1.15.1 which may be useful for melting and alloying operations. The data of Table 1.15.1 are supplemented in Table 1.15.2 by the 1945 data of C. S. Smith.¹

Tables 1.15.3 through 1.15.8 represent the most recently declassified data from the Los Alamos Scientific Laboratory.

HEALTH HAZARDS

The health hazard involved in handling plutonium is a consequence of its natural radioactivity. Plutonium is an alpha-particle emitter, the particles having an energy of 5.15 mev and a range of 3.68 cm in air. Because of their large mass and charge, alpha particles have very little penetrating power. The range of the plutonium alpha particle in body tissue is only about 45 microns. The damage caused by these particles occurs when plutonium is taken into the body. Because of their small penetrating power, the emitted particles dissipate their entire energy in the tissues immediately surrounding the point of plutonium deposition.

¹References appear at end of chapter.

Table 1.15.1 — Physical Constants of Plutonium

Density,* gm/cm ³	
Alpha Pu, 25°C	19.60 ± 0.02
Liquid, 665°C	16.54 ± 0.08
Melting point, °C	632 ± 7
Heat of vaporization, kcal/mole	80.46 ± 0.34
Vapor pressure, mm Hg	
$\log_{10} P = \frac{-(17,587 \pm 73)}{T(^{\circ}\text{K})} + (7.895 \pm 0.047)$	
Coefficient of linear expansion, per °C	
Alpha Pu, -180° to 100°C	
$\alpha = \left(\frac{1}{L_0}\right) \frac{dL}{dt} = (48.39 \pm 0.01) \times 10^{-6} + (0.0959 \pm 0.002) \times 10^{-6} t(^{\circ}\text{C})$	
* Gm/cm ³ × 62.43 = lb/cu ft	

Table 1.15.2 — Properties of Plutonium Metal¹
(1945 Values, Approximate)

Phase	Temperature range of stability, °C	Crystal structure	Density* at 25°C, gm/cm ³	Average linear expansion coefficient, per °C	Electrical resistivity, μohm-cm	Temperature coefficient of resistivity
Alpha	Below-117	Orthorhombic like uranium (doubtful)	19.8	55 × 10 ⁻⁶	150 at 25°C	-29.7 × 10 ⁻⁴
Beta	117 to 200	Unknown (complex)	17.8	35 × 10 ⁻⁶	110 at 200°C	0 (approx.)
Gamma	200 to 300	Unknown (complex)		36 × 10 ⁻⁶	110 at 300°C	0 (approx.)
Delta	300 to 475	Face-centered cubic	16.0	-21 × 10 ⁻⁶	102 at 400°C	+1.5 × 10 ⁻⁴
Epsilon	475 to 637	Body-centered cubic	16.4	4 × 10 ⁻⁶	120 at 500°C	0 (approx.)

*Gm/cm³ × 62.43 = lb/cu ft

Table 1.15.3—Typical Plutonium Metal Purities

Material	Total Plutonium	
	Weight-%	Atomic-%
Earlier Material	99.87	99.01
High-Purity Sample No. 1	99.97	99.82
High-Purity Sample No. 2	99.95	99.75

Table 1.15.4—Phase-Transformation Data on Plutonium Metal

Transformation	Temperature°C*		ΔV , %†
	Dilatometer	Thermal Analyses	
$\alpha - \beta$	122 ± 2	122	8.9
$\beta - \gamma$	206 ± 3	203	2.4
$\gamma - \delta$	319 ± 5	317	6.7
$\delta - \delta'$	451 ± 4	453	-0.4
$\delta' - \epsilon$	476 ± 5	477	-3.0
$\epsilon - \text{Liq.}$		639.5 ± 2	

*On Heating Only

† $\Delta V = (v_2 - v_1)/v_1$

Table 1.15.5—Crystal Structure Data on High-Purity Plutonium Metal

				Density, gm/cm ³
Gamma: Face-Centered Orthorhombic				
At 210°C	a ₀ = 3.1603Å	b ₀ = 5.7624	c ₀ = 10.141	17.19
Delta: Face-Centered Cubic				
At 320°C	a ₀ = 4.6370			15.92
Delta-Prime: Face-Centered Tetragonal				
At 465°C	a ₀ = 4.701	c ₀ = 4.489	c/a = 0.955	15.99
Epsilon: Body-Centered Cubic				
At 500°C	a ₀ = 3.638			16.48

Table 1.15.6—Inter-Atomic Distances in Plutonium Metal Structures

Phase	Structure	Coordination	Distances	Temperature, °C
Gamma	Orthorhombic	10	4 Pu 3.021 Å	210
			2 Pu 3.160 Å	210
			4 Pu 3.286 Å	210
			Ave. 3.155 Å	210
Delta	Cubic F. C.	12	3.279 Å	320
Epsilon	Cubic B. C.	8	3.150 Å	500

Table 1.15.7—Phase Data*

Phase	Density, gm/cm ³	Coefficient† of Linear Expansion, 10 ⁻⁶ per °C	Resistivity, $\rho \times 10^6$	$1/\rho \cdot d\rho/dt \times 10^5$
α	19.737 (25°)	50.8 (25°)‡	145 (28°)	-21
β	17.65 (150°)	38.0 (164°)‡	110.5 (132°)	-6
γ	17.19 (210°)	34.7 (ave.)‡	110 (230°)	-5
δ	15.92 (320°)	-10.0 \pm 0.5	103 (353°)	+7
δ'	15.99 (465°)	-120	105 (462°)	+45
ϵ	16.48 (500°)	25.7 \pm 2.0	114 (490°)	-7
Liquid	16.50 (665°) \pm 0.08	50§		

*t = °C

† $\frac{1}{L} \cdot \frac{\Delta L}{\Delta t} = \alpha$

‡See Table 1.15.8

§Volume Coefficient

Table 1.15.8—Expansion Coefficients of α , β and γ Phases of Plutonium Metal*

Alpha (-180° to +122°C)

$$\alpha \times 10^6 = (48.39 \pm 0.01) + (0.0959 \pm 0.0012)t$$

Beta (82 to 206°C)

$$\alpha \times 10^6 = (26.04 \pm 0.01) + 0.0740 \pm 0.0015)t$$

Gamma ($\alpha \times 10^6$ in each case) (149 to 319°C)

$$\alpha_{[100]} = -19.7 \pm 1.7; \alpha_{[010]} = 39.5 \pm 0.9; \alpha_{[001]} = 84.3 \pm 2.3$$

$$\alpha_{\text{Ave.}} = 34.7 \pm 3.0$$

*t = °C

The maximum permissible body burden (in bone) for plutonium is currently defined as 0.04 microcurie, or 0.5 microgram.² Plutonium entering the body is deposited primarily in the bones and is excreted very slowly; the time required for man to excrete one-half his body burden is estimated to be about 100 years. Any laboratory working with plutonium should have facilities for the detection of plutonium in urine. Based on an average urinary excretion rate of 0.01 percent of the body content per day, the maximum permissible body burden (0.04 microcurie) is equivalent to 7 disintegrations (counts)/min in a 24-hr urine sample.³

Plutonium may enter the body in three different ways:

1. Inhalation and absorption through the lungs.
2. Ingestion and absorption from the gastrointestinal tract.
3. Absorption through the skin.

Of these, inhalation is the most important. Current research indicates that, for soluble compounds of Pu^{239} , about 10 percent of the inhaled amount is retained. The mean life of insoluble compounds in the lungs is considered to be 200 days. Maximum permissible concentrations in air are based on the retention and absorption of the soluble compounds.⁴

Because of the ease with which ingress to the gastrointestinal tract can be controlled and the low absorption rate (about 0.01 percent), the absorption of Pu^{239} from the gastrointestinal tract is a minor health problem.

Because of their low penetrating power, Pu^{239} alpha particles do not cause radiation damage to the skin. Care must be taken, however, to see that plutonium compounds are not absorbed into the skin from organic solvents which have them in solution. Plutonium may enter the body tissues through breaks in the skin. It is standard laboratory practice not to allow personnel with open wounds on the hands or wrists to work with plutonium or its compounds. Injuries which result in the skin being broken by objects contaminated with plutonium should receive prompt medical attention.

Plutonium metal (a mixture of isotopes) emits low-energy gamma and X-ray radiation. In normal chemical operations, the shielding provided by containers and the short handling periods prevent undue hand exposure. In handling plutonium metal, however, this type of radiation may become serious. The dosage rate of bare plutonium metal through neoprene gloves of 0.025-in. thickness normally used in this type of operation is approximately 0.9 rep/hr (rep = roentgen equivalent physical), but the rate may vary considerably with small variations in glove thickness.⁵

Some plutonium alloys and compounds of light elements produce neutrons. Such materials must be handled according to the same health precautions required for any other neutron source.

The following general rules for handling plutonium in research and production operations have been prescribed by the Health Division of the Los Alamos Scientific Laboratory. In order to comply with the urine tolerance mentioned above, the word "should," wherever it appears, must be understood to mean "must."

1. Rubber surgeon's gloves should be worn when handling more than one microgram of plutonium.
2. Work with plutonium should be carried out in enclosures such as dryboxes or hoods. Work with solid compounds or the metal requires dryboxes; some wet chemistry operations involving low concentrations of plutonium may be safely carried out in hoods, provided the minimum air flow across the face of the hood is at least 125 linear feet per minute.
3. The maximum allowable concentration of air-born plutonium is $2 \times 10^{-12} \mu\text{c/ml}$. This concentration is calculated on the basis of 168 hours per week exposure with a breathing rate of 1.25×10^6 ml per hour of working time and 0.63×10^6 ml per hour of off time. If exposure is during working hours only, permissible concentrations may be increased accordingly.⁶

4. When the air-borne concentration is expected to exceed the maximum permissible concentration, respirators and "full protective clothing" should be worn. Respirators should have a high filtering efficiency for particles of less than 10-micron diameter.
5. No mouth-pipetting operations should be carried out with plutonium solutions.
6. No glass blowing should be done on equipment contaminated with plutonium.
7. Personnel should wear protective clothing, such as laboratory coats or coveralls while working in plutonium laboratories. "Full protective clothing" consists of a complete change of clothing with coveralls for outer cover.
8. Surface contamination of laboratory furniture and equipment must be kept at a minimum. Experience has shown a satisfactory tolerance level to be 1000 disintegrations per minute for 75 cm² of area.
9. Exhaust air from hoods and dryboxes should be filtered. Such filters should have a high efficiency for particles of less than 10-micron diameter.
10. Waste materials and equipment contaminated with plutonium should be segregated and disposed of in such a manner that the plutonium will not become air-borne or enter into ground water.
11. Plutonium-contaminated liquid wastes should not be discharged into sanitary sewers; such effluent should be treated to reduce the plutonium content to a safe level. The maximum permissible concentration of plutonium in drinking water is 1.5×10^{-6} $\mu\text{c}/\text{ml}$.
12. Maintenance work on equipment used to handle plutonium should be done under the supervision of personnel trained in the control of radiological health hazards.
13. Periodic urinalyses for plutonium should be run on personnel involved in routine handling of larger than microgram quantities of plutonium.

Space limitations do not permit a detailed exposition of routines that must be established, equipment elaborations that must be made, unusual laboratory servicing that must be provided, and other expenditures of time and money necessary to work with plutonium in full compliance with these rules. Some idea of such considerations is suggested later in this chapter in discussions of contamination problems and methods used to minimize them in relation to a particular plutonium technology. In addition to the urine counts which, depending on degree of exposure, are required at intervals ranging from biweekly to semiannually (plus special counts for accidents), nose counts are usually taken daily, and hand counts at frequent intervals are important during and at the end of each half-day of work.

Because plutonium is a heavy metal and forms heavy compounds, the usual design of chemical hoods, or other ventilating equipment for chemical fumes, has not been satisfactory in exhausting plutonium-contaminated air. In such equipment, provision is ordinarily made for air to be removed in an upward direction, as into the outer atmosphere through a roof. Experience has demonstrated that in this type of installation, plutonium compounds tend strongly to gravitate back to their point of origin. An obvious solution to the problem which has proved very effective in practice is to employ a downward direction for the flow of exhaust air, at least at the point where it leaves the ventilated enclosure.

The known data on a number of binary compounds of plutonium are presented in Table 1.15.9.

Table 1.15.9—Binary Alloys of Plutonium

System	Features of the phase diagram	Intermediate phases			
		Composition	Crystal structure	Unit cell dimensions, Å	Molecules/unit cell
Pu-C	None known	PuC	F.c.c., NaCl type	$a_0 = 4.919$	4
		Pu_2C_3	B.c.c.	$a_0 = 8.129$	8
Pu-H	None known	$(\text{PuH}_2\text{-PuH}_3)$	F.c.c., CaF_2 type	PuH_2 :	4
			Hexagonal	$a_0 = 6.820$	2
				PuH_{2-3} :	
Pu-N	None known	PuN	F.c.c., NaCl type	$a_0 = 3.75\text{Å}$	4
Pu-O	None known	PuO	F.c.c., NaCl type	$a_0 = 6.80\text{Å}$	4
		Pu_2O_3	F.c.c., NaCl type	$a_0 = 4.904$	4
		Pu_2O_3	B.c.c., Mn_2O_3 type	$a_0 = 9.962$	16
		Pu_2O_3	Hexagonal, La_2O_3 type	$a_0 = 11.047$	1
		PuO_2	Hexagonal, La_2O_3 type	$a_0 = 3.82$	1
Pu-Si		PuO_2	F.c.c., CaF_2 type	$c_0 = 5.94$	4
		PuSi_2	F.c.c., CaF_2 type	$a_0 = 5.395$	4
		PuSi_2	Tetragonal, USi_2 type	$a_0 = 3.97$	4
Pu-S		PuSi_2	Tetragonal, USi_2 type	$c_0 = 13.55$	4
		Pu-S	F.c.c., NaCl type	$a_0 = 5.536$	4
Pu-S		Pu_2S_3	F.c.c., NaCl type	$a_0 = 5.536$	4
		Pu_2S_3	Ce_2S_3 type	$a_0 = 8.4543$	4

REFERENCES

1. C. S. Smith, "Metallurgy at Los Alamos, 1943-1945," *Metals Progress*, pp 81-89, May, 1964.
2. National Bureau of Standards Handbook No. 47.
3. Health Division of Los Alamos Scientific Laboratory.
4. Chalk River Permissible Dose Conference, September, 1949.
5. Health Division of Los Alamos Scientific Laboratory.
6. AEC Division of Biology and Medicine, and National Bureau of Standards Handbook No. 47.

CHAPTER 1.16

Rare Earths

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Because of their similar properties and associated occurrence in nature, elements 21, 39, and 57 through 71 are considered here as rare earths. The above-noted elements are listed in Table 1.16.1.

Table 1.16.1—The Rare Earths

Name	Symbol	Atomic No.
Scandium	Sc	21
Yttrium	Yt	39
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sa	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71

REACTOR APPLICATION

The application of rare earths in nuclear reactors will probably be for control purposes. Some of the rare earths have the highest thermal-neutron cross sections of any of the elements. Gadolinium, in particular, has a thermal absorption cross section of 44,000 barns. In addition, the cross sections of some of the heavier rare earths do not decrease as rapidly with increasing neutron energy as in other elements.

ABUNDANCE AND AVAILABILITY

Estimated abundances of the rare earths are given in Table 1.16.2. Thus cerium, the most plentiful "rare" earth, is more abundant than such "common" elements as tin, mercury, cadmium, antimony, bismuth, and tungsten.

Monazite sands have been the most important source of the rare-earth materials. Recently, large deposits of bastnasite have been found in California. These deposits promise to be an important source of the rare earths. Gadolinite, a Scandinavian ore, is a rich source of the heavy rare earths.

Misch metal, an alloy of variable composition containing all the rare earths in the proportions in which they occur in the ores and up to 5 percent iron, is readily available in ton lots. Some 900 tons per year is being produced at present.

Table 1.16.2 — Estimated Abundance of Rare-earth Metals

(D. M. Yost, H. Russell, Jr., and C. S. Garner,
"The Rare Earth Elements and Their Compounds,"
John Wiley & Sons, Inc., New York, 1947)

Rare earth	Estimated percentage of earth's crust	Rare earth	Estimated percentage of earth's crust
Lanthanum	0.00035	Terbium	0.00005
Cerium	.00155	Dysprosium	.00035
Praseodymium	.00025	Holmium	.00005
Neodymium	.00090	Erbium	.00030
Promethium	.00000	Thulium	.00005
Samarium	.00035	Ytterbium	.00035
Europium	.00001	Lutetium	.00007
Gadolinium	.00035		
		Total	0.005

Cerium is the easiest of the rare earths to separate. It is available in fairly pure form in ton lots and in spectrographic purity in pound lots.

Lanthanum, neodymium, and praseodymium are also available in pound lots, but the other rare earths, except for promethium, which is practically nonexistent in nature, have been produced only in gram or milligram lots.

In 1948 the relative costs of these materials were:

Misch metal	\$ 4.00/lb
Cerium	50.00/lb
Lanthanum	175.00/lb
Neodymium	200.00/lb
Praseodymium	750.00/lb

The price of the separated metals, notably cerium, has decreased somewhat since that time.

EXTRACTION AND PURIFICATION

PRODUCTION OF MISCH METAL

Misch metal, the mixed rare-earth metal of commerce, is prepared by electrolytic methods. The source material is the residue of the ores remaining after thorium remov-

al. This is converted to the chloride, which is then purified and electrolyzed. Sodium or calcium chloride is added to prevent metal fog and to improve electrical conductivity. The electrolysis is usually carried out batchwise in a fire-clay-lined iron cylinder. A round graphite or iron bar at the bottom is used as the cathode, and a graphite anode is placed at a distance of 25 cm. If boron contamination is not desired, molybdenum or tantalum cathodes can be used. Electrode sizes are such that current densities of 6 to 10 amp/sq cm at the cathode and 1 to 2 amp/sq cm at the anode can be used.

To start the cell, a small graphite rod is shorted across the electrodes until the salt melts and is sufficiently conductive. Electrolysis is started with a rare-earth chloride-calcium chloride mix, then gradually altered toward pure rare-earth chloride. Alternatively, an electrolyte containing 85 percent rare-earth chloride and 15 percent KCl-NaCl eutectic can be used. Electrolysis is carried out at 1560°F. Too low a temperature results in spongy metal, and too high a temperature produces metal fog which interferes with the electrolysis. Metal yield is 40 to 65 percent. The anode is raised as electrolysis continues, and finally the molten metal is poured out of the cell. In continuous operating cells, metal is tapped out periodically at intervals that may be as long as 100 hr.

SEPARATION OF THE RARE EARTHS

Historically, there were two groups of rare earths: "ceria," containing the oxides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium; and "yttria," containing the oxides of yttrium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. It was originally believed that "ceria" and "yttria" were pure substances. Although the complexity that is indicated above exists and the separation indicated above is not so clear-cut, it is convenient to maintain this two-group classification.

A fractional crystallization method of separation has been used in the past. A scheme for this is given in Table 1.16.3. This fractional crystallization technique is long and tedious and, as a complete method, has been superseded by ion-exchange methods. It is still of interest, however, because it will be used in preliminary steps to produce feed solutions for the ion-exchange process. Cerium separation from the other rare earths is relatively simple by the oxidation-precipitation method indicated and is quite adequate.

Scandium, usually present with the rare earths, appears with the "yttria" group if it is not previously removed. It can be removed by precipitating the rare-earth fluorides in strong ammonium bifluoride solutions. The scandium forms a soluble complex fluoride ion and remains in solution.

Yttrium, although it gives its name to the heavy rare-earth group for historical reasons, is not a true rare earth. It is present, however, and has many similar properties. It is removed in the fractional crystallization step by a ferrocyanide precipitation. It remains in solution.

Ion-exchange techniques have recently been adapted to rare-earth separations. They offer faster and more efficient separation than the fractional-crystallization and precipitation method. The preferred technique is to adsorb the rare-earth ions on Amberlite or some other high-capacity resin bed and then to elute them with citric acid solutions (0.5 to 1.0 percent citric acid adjusted to appropriate pH with NH_4OH).

Several chemical methods can be used in conjunction with the ion-exchange process (or with the fractional crystallization process). Already mentioned is the removal of cerium by oxidation and precipitation as $\text{Ce}(\text{OH})_4$.

The formation of PrO_2 can be used to separate praseodymium from lanthanum by a nitrate fusion process. The presence of CeO_2 as a carrier for PrO_2 is desirable in this process.

The divalent states of samarium, europium, and ytterbium are useful in separating these elements for the heavier rare earths beginning with gadolinium. These three ele-

Table 1.16.3 — Separation of the Rare-earth Elements

(D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare-earth Elements and Their Compounds," John Wiley & Sons, Inc., New York, 1947)

Thorium-free residue from monazite sands in Cl^- or NO_3^- solution
Oxidize with NaClO and add NaOH

Precipitate: mainly Ce(OH) ₃ Dissolve in HNO ₃ and H ₂ O ₂ solution If Nd or Pr absorption bands are present, repeat procedure Solution: Ce ⁺³ Purify Ce ⁺³ by fractional crystallization as Mg cerous nitrate Pure Ce	Filtrate: other rare-earth ions Add NH ₃ , NH ₄ NO ₃ , and Cd(NO ₃) ₂ [presence of Cd(NO ₃) ₂ appears to make separation cleaner]; filter precipitate; repeat procedure until filtrate shows no Nd or Pr absorption lines Precipitate: hydroxides of rare earths except Ce and La Dissolve precipitate in HNO ₃ Solution: rare-earth ions except La ⁺³ and Ce ⁺³ By additions of NH ₃ and NH ₄ NO ₃ , precipitate fractionally small amounts of the rare-earth hydroxides					Filtrate: La ⁺³ Precipitate Cd ⁺² with H ₂ S; discard precipitate; purify La ⁺³ by fractional crystallization as magnesium lanthanum nitrate Pure La
	Head fractions: colorless precipitate of Lu, Yb hydroxides (Th and Sc appear here if they have not been removed completely) Yttrium-group fractions (see below)	Middle fractions: Tm, Ho, Er, Yt, Dy, Tb, Gd hydroxides, some Eu and Sa hydroxides	End fractions: Pr ⁺³ , Nd ⁺³ , Eu ⁺³ , Sm ⁺³ , some La ⁺³ , and Gd ⁺³ Make magnesium double nitrate fractional crystallizations	End fractions: yellow solutions of Sm ⁺³ , Eu ⁺³ , some Nd ⁺³ and Gd ⁺³ Continue magnesium double nitrate fractional crystallization	Pure Eu	
		Head fractions: green solution of La ⁺³ , some Pr ⁺³ , and no Nd ⁺³ Separate La ⁺³ by basic precipitation method used above Pure Pr	Middle fractions: rose solutions of Nd ⁺³ , some Sm ⁺³ , and Pr ⁺³ Continue magnesium double nitrate fractional crystallizations Pure Nd	Head fraction: Sm ⁺³ Continue magnesium double nitrate fractional crystallization Pure Sa		
						Fractions containing Eu ⁺³ , Sm ⁺³ , and some Gd ⁺³ Electrolyze sulfate solution Precipitate: EuSO ₄ , some Gd(OH) ₃ Dissolve with HNO ₃ , reduce with zinc, and add conc samarium fractions HCl to precipitate EuCl ₃
Yttrium-group fractions: Yt, Gd, Tb, Dy, Er, Ho, Tm, Yb, Lu, and some cerium-group hydroxides Dissolve each fraction in dilute nitric acid; add powdered Na ₂ SO ₄ to the warm, well-stirred solution until the strong absorption line of Nd is not detectable in the solution Solutions: yttrium-group elements Add warm conc K ₃ Fe(CN) ₆ solution to the neutral solutions until the absorption lines of Ho and Er have disappeared from the solutions						
Precipitate: cerium-group sulfates Add to previous cerium-group samples	Precipitates: ferricyanides of yttrium group in various fractions; most of yttrium removed Treat precipitates with conc NaOH solution, add much water, and filter the resulting hydroxides; dissolve in HNO ₃ or HCl and repeat procedure; fractionally crystallize the bromates					
	Head fractions: Gd ⁺³ , Tb ⁺³ , some Nd ⁺³ , Eu ⁺³ , and Sa ⁺³	Middle fractions: Tb ⁺³ , some Gd ⁺³ , and Dy ⁺³	Middle fractions: Dy ⁺³ , some Tb ⁺³ , Ho ⁺³ , and Yt ⁺³	Middle fractions: Ho ⁺³ , Er ⁺³ , some Yt ⁺³ , and Dy ⁺³	End fractions: Tm ⁺³ , Yb ⁺³ , Lu ⁺³ , and some Er ⁺³ and Ho ⁺³ E	
Solution: Yt ⁺³ Add NaOH Precipitate: Yt(OH) ₃ Dissolve in HNO ₃ or HCl and test for absorbing elements (Nd, Ho, Er); repeat procedure if they are present; purify yttrium by fractional crystallization of the bromate Pure Yt					Pure Yt	

Table 1.16.3 — (Continued)

A. Solution: Gd^{+3} , Tb^{+3} , and some Nd^{+3} , Eu^{+3} , and Sm^{+3} Precipitate: $Nd_2(SO_4)_3$; $Sm_2(SO_4)_3$ Combine with previous neodymium and samarium fractions		Solution: Gd^{+3} , Tb^{+3} , some Eu^{+3} ; electrolyze sulfate solution	
Precipitate: $EuSO_4$ Combine with previous europium fractions		Solution: Gd^{+3} , Tb^{+3} ; fractionally crystallize the bromates	End fractions: Tb^{+3}
B. Solution: Tb^{+3} , some Gd^{+3} , and Dy^{+3} Fractionally crystallize from hot, weakly ammoniacal concentrated solution of ammonium oxalate		Head fractions: Pure Gd	Combine with other terbium fractions
Head fraction: Gadolinium ammonium oxalate; combine with previous gadolinium fractions		Middle fraction: Tb^{+3} Pure Tb	End fraction: Dy^{+3} (Combine with other dysprosium fractions)
C. Solution: Dy^{+3} , some Tb^{+3} , Ho^{+3} , Y^{+3} Fractionally crystallize the bromates		End fractions: Dy^{+3} Combine with other holmium fractions	
Head fractions: Tb^{+3} Combine with previous terbium fractions		Middle fractions: Dy^{+3} Pure Dy	
D. Solution: Ho^{+3} , Er^{+3} , some Y^{+3} , and Dy^{+3} Fractionally crystallize the bromates		End fractions: Ho^{+3} Combine with other holmium fractions	
Head fractions: Dy^{+3} , some Ho^{+3} Combine with dysprosium fractions		Middle fraction: Ho^{+3} , Yt^{+3} , and Er^{+3} Fractionally crystallize the basic nitrates by converting $\frac{1}{2}$ of the salt to the oxide and then dissolving the oxide in a rather conc nitrate solution heated to boiling; cool	
Head fractions: Yt^{+3} Add to previous yttrium fractions		Middle fractions: Yt^{+3} , Ho^{+3} , Er^{+3} Fractionally crystallize bromates and add to appropriate fractions	
Head fractions: Yt^{+3} Add to previous yttrium fractions		End fractions: Er^{+3} some Y^{+3} , and Ho^{+3} Fractionally crystallize the bromates or the ammonium double oxalates	
E. Solution: Tm^{+3} , Yb^{+3} , Lu^{+3} , and some Er^{+3} and Ho^{+3} Fractionally crystallize the ammonium double oxalates as described in B		Pure Er	
Head fraction: Er^{+3} and Ho^{+3} Add to erbium and holmium fractions		Middle fractions: Yb^{+3} , Tm^{+3} , Lu^{+3} Electrolyze the sulfate solution	
Middle fraction: Tm^{+3} Pure Tm		End fractions: Lu^{+3} Pure Lu	
Precipitate: $YbSO_4$, traces of Tm^{+3} and Lu^{+3} Purify by repeated electrolysis or by ammonium double oxalate fractional crystallization		Solution: Tm^{+3} , Lu^{+3} Fractionally crystallize the ammonium double oxalates	
Pure Yb		End fraction: Lu^{+3} Add to other lutetium fractions	

ments in acid acetate solution pass into the mercury when shaken with dilute sodium amalgam. The lighter rare earths (up to gadolinium) also enter into a similar reaction but not so strongly. This probably indicates a divalent state of low stability for these elements. The rare earths that enter the mercury can be removed subsequently by water or dilute HCl treatment. To get complete separation by this method is also tedious but faster than the crystallization process.

A more efficient method of separation of samarium, europium, and ytterbium from the other rare earths was discovered accidentally during attempts to produce samarium metal by calcium reduction of the trichloride. No metal is formed, only the dichloride. When mixtures of gadolinium and samarium trichlorides were reduced, all the samarium remained in the slag. Supposedly, samarium, europium, and ytterbium could also be removed from the light rare earths by this method, since these metals are readily produced by calcium reduction of their trichlorides.

Preliminary experiments with solvent extraction as a method for separating the rare earths indicate that it may become increasingly important and may even replace the ion-exchange method.

When gadolinium and samarium oxides were coreduced with zirconium at temperatures of 2900° to 3100°F, the samarium distilled off first. This offers another possible separation method, though an expensive one.

PREPARATION OF INDIVIDUAL RARE-EARTH METALS

Electrolytic methods, similar to that described for misch metal, can be and are used for the production of the individual metals. With proper precautions and refined equipment, metal of suitable purity can be produced electrolytically. However, high-purity metal is produced more easily, with the exception of samarium, europium, and ytterbium, by calcium reduction of the purified anhydrous chlorides. This can be done in magnesia-lined steel bombs. Iodine is added to the mix along with excess calcium to give sufficient excess heat to consolidate the metal and get good separation. It is necessary to operate about 400° to 575°F above the melting point to get massive metal. For example, it is necessary to go to 2370°F with gadolinium. At 1470°F, powder is formed.

For especially high-purity metal, tantalum equipment can be used. There appears to be no reaction between tantalum and the rare earths, at least at 2370°F.

Excess calcium and other volatile impurities in the "biscuits" are removed by vacuum melting at about 2550°F and casting from magnesia or tantalum crucibles.

Calcium reduces the trichlorides of samarium, europium, and ytterbium only to the divalent state instead of to metal. However, some success has been had using barium as the reducing agent for these metals. Calcium reduction of these three metals in the presence of a large amount of zinc will give very dilute alloys.

PHYSICAL AND CHEMICAL CONSTANTS

Tables 1.16.4 and 1.16.5 give some of the physical, chemical, and thermodynamic constants of the rare-earth metals.

CRYSTALLOGRAPHY

Table 1.16.6 gives the crystal form and lattice structure of the rare earths.

ALLOTROPIC TRANSFORMATIONS

Allotropic forms have been reported for scandium, cerium, lanthanum, praseodymium, and possibly erbium. The transitions are sluggish and depend on the previous history of

Table 1.16.4 — Physical and Chemical Constants of the Rare-earth Metals

Element	Thermal-neutron-absorption cross section, barns/atom	Density,* gm/cm ³	Melting point, °C	Boiling point, °C	Heat of fusion, kcal/mole	Heat of vaporization, kcal/mole
Scandium	13 ± 2	2.5	1400	...	4	93
Yttrium	1.38 ± 0.14	5.51	1475	...	4	103
Lanthanum	8.9 ± 0.3	α 6.194 β 6.18	866 ± 10	4340 ± 260	2.3	79.5 ± 1.7
Cerium	0.70 ± 0.08	α 6.78 β 6.81	780 ± 10	2420 ± 70	5.5	107.7 ± 2
Praseodymium	11.2 ± 0.6	α 6.776 β 6.805	950 ± 10	3020 ± 90	3.1	79.5 ± 1.1
Neodymium	44 ± 2.0	6.998	820 ± 10	36
Promethium
Samarium	6500 ± 1000	6.93	>1300
Europium	4500 ± 500	5.224
Gadolinium	44,000 ± 2000	7.948	~1200
Terbium	44 ± 4	8.332	>1400
Dysprosium	1,100 ± 150	8.562	1400
Holmium	64 ± 3	8.764	~1200
Erbium	166 ± 16	9.164	>1140
Thulium	118 ± 6	9.346	>1400
Ytterbium	36 ± 4	7.010	~1800
Lutetium	108 ± 5	9.740

*Gm/cm³ × 62.43 = lb/cu ft

the metal. For example, a cerium rod, cast and turned, showed a mixed face-centered cubic and hexagonal close-packed structure at room temperature. A similar rod, extruded and turned, was entirely face-centered cubic. Lanthanum rod, cast and turned, was hexagonal close packed with some face-centered cubic. A similar extruded and turned lanthanum rod was also hexagonal close packed with some face-centered cubic. A cast and turned praseodymium rod was hexagonal close packed with a small amount of body-centered cubic, and a similar neodymium bar was entirely hexagonal close packed.

The sluggishness of the transitions makes it difficult to determine the exact transition temperature.

MECHANICAL PROPERTIES

The mechanical properties of the rare earths have not been extensively examined. One sample of rolled cerium was reported to have an ultimate tensile strength of 12,900 lb/sq in. Hardness for this particular specimen was 42 Brinell (500-kg, 10-mm ball).

Hardnesses of the rare earths are compared with those of some better known metals in the following list, which is in the order of increasing hardness: lead, tin, cerium, lanthanum, zinc, neodymium, praseodymium, gadolinium, and mild steel.

A sample of as-cast cerium had a hardness of 60 Rockwell "M" (¼-in. ball, 100-kg load). The same material cold rolled 25 percent had a hardness of 92 R_M. No further increase in hardness was noted with additional cold work.

Brinell measurements (500-kg, 10-mm ball) gave values as follows on high-purity metal, as cast: Ce-19, Nd-33.

Table 1.16.5 — Thermodynamic Constants of the Rare Earths

Specific heat, cal/(mole)(°K)

Lanthanum

298° to 800°K

$$C_p = 6.17 + 1.60 \times 10^{-3}T$$

Cerium

298° to 800°K

$$C_p = 4.40 + 6.00 \times 10^{-3}T$$

Praseodymium

293° to 373°K

$$C_p = 6.85$$

Neodymium*

0° to 400°C

$$C_p^\dagger = 6.479 + 7.065 \times 10^{-3}t + 4.463 \times 10^{-6}t^2$$

Enthalpy, or heat content, cal/mole

Lanthanum†

298° to 800°K

$$H_T - H_{298.15} = 6.17T + 0.80 \times 10^{-3}T^2 - 1911$$

Cerium‡

298° to 800°K

$$H_T - H_{298.15} = 4.40T + 3.00 \times 10^{-3}T^2 - 1579$$

Praseodymium

293° to 373°K

$$H_T - H_{298.15} = 6.85T - 2042$$

Neodymium*

0° to 400°C

$$H_t - H_0 = 6.479t + 3.533 \times 10^{-3}t^2 + 1.488 \times 10^{-6}t^3$$

Entropy at 25°C., cal/(mole)(°C)

CeriumLanthanumLutetium

Solid

13.8 ± 0.8

13.7 ± 0.8

14.5

Gas

48.09 ± 0.05

43.57 ± 0.01

Entropy ($S_T - S_{25^\circ\text{C}}$) cal/(mole)(°C)Temp., °CCeriumLanthanumNeodymium

127

1.93

1.96

2.18

227

3.51

3.52

3.97

327

4.90

4.80

5.54

427

6.18

5.92

6.94

527

7.36

6.88

8.22

627

...

...

9.41

Vapor pressure, mm Hg

Lanthanum

$$\log P = \frac{-17,185 \pm 372}{T} + 6.605 \pm 0.201$$

Cerium

$$\log P = \frac{-23,400 \pm 440}{T} + 11.58 \pm 0.27$$

Praseodymium

$$\log P = \frac{-17,188 \pm 243}{T} + 8.098 \pm 0.156$$

Samarium,

Reported to have higher vapor pressure than gadolinium in range 1600° to 1700°C

Electrical resistivity

(room temperature), $\mu\text{ohm-cm}$

Lanthanum

65 – 75

Cerium

75 – 90

Praseodymium

75

Neodymium

70

*t = °C

†Formula accurate within 2 percent

‡Formula accurate within 3 percent

Table 1.16.6—Crystal Form and Lattice Structure of the Rare Earths

Element	Crystal form*	Lattice constants, A	
		a ₀	c ₀
Scandium (α)	F.c.c.	4.541	...
Scandium (β)	H.c.p.	3.309	5.256
Yttrium	H.c.p.	3.637	5.762
Lanthanum (α)	F.c.c.	5.305	...
Lanthanum (β)	H.c.p.	3.762	6.075
Cerium (α)	F.c.c.	5.150	...
Cerium (β)	H.c.p.	3.657	5.972
Praseodymium (α)	H.c.p.	3.660	5.920
Praseodymium (β)	B.c.c.	5.161	...
Neodymium	H.c.p.	3.657	5.902
Promethium	F.c.c.
Samarium	H.c.p.
Europium	B.c.c.	4.582	...
Gadolinium	H.c.p.	3.629	5.760
Terbium	H.c.p.	3.592	5.675
Dysprosium	H.c.p.	3.585	5.650
Holmium	H.c.p.	3.564	5.631
Erbium	H.c.p.†	3.539	5.600
Thulium	H.c.p.	3.530	5.575
Ytterbium	F.c.c.	5.479	...
Lutetium	H.c.p.	3.516	5.570

*F.c.c., face centered cubic; h.c.p., hexagonal close-packed;
b.c.c., body-centered cubic

†Other structures have been reported

A Rockwell "H" value ($\frac{1}{16}$ -in. ball, 60-kg load) of 55 is the lowest measured for high-purity as-cast lanthanum.

MELTING AND CASTING

The attack of various rare-earth metals on crucible materials is shown in Table 1.16.7.

Magnesia has probably been most widely used as crucible material for melting the rare-earth metals. Tantalum is desirable and very satisfactory where higher purity is desired, but it has not yet been applied to large-size melting operations. It is necessary to degas tantalum crucibles and molds at 2550°F prior to use. Crucibles of La_2O_3 and CaO are undesirable because they slake in air, and beryllia crucibles are not popular because of the health hazard involved with their use. Titanium nitride crucibles have been successful with gadolinium but had to be destroyed after each melt.

Temperatures of 200° to 400°F above the melting point of the metal are desirable for satisfactory casting. In magnesia crucibles an even higher superheat may be necessary because of the tough oxide skin that is formed on the molten metal.

FORMING AND FABRICATION

Forging, rolling, both hot and cold, and extrusion operations have been successful on those rare-earth metals on which they have been tried. There seems to be no reason why

Table 1.16.7 — Attack of Rare-earth Metals on Various Crucible Materials

Metal	Temperature, °F, at which attack begins on crucible material					
	BeO	CaO	La ₂ O ₃	MgO	Ta	Mo
Cerium	No attack, <2000	Attack, 2100	...	No attack, <2190	No attack, <3090	No attack, <2550
Didymium*	...	Mild attack, >1650	...	No attack, <2000	No attack, <2460	No attack, <2460
Lanthanum	No attack, <2100	Mild attack, >2280	1100	...	No attack, <2190	...
Neodymium	...	Mild attack, >1650	...	No attack, <2190	No attack, <3000	...
Praseodymium	No attack, <2100	No attack, <2190	...
Gadolinium	No attack, <2370	No attack, <2370	...
Dysprosium	No attack, <2550	...
Erbium	No attack, <2550	...
Yttrium	No attack, <2100	No attack, <2730	...

*Mixture of neodymium and praseodymium

they cannot be applied to all the rare earths. Protection from reaction with oxygen and nitrogen is necessary. Cladding is most generally used for this purpose.

With cold working, cerium work hardens at about 25 percent cold reduction, but hardening does not continue beyond that point. This is a lower limit than for most metals.

Gadolinium can be cold worked several percent, but hot rolling at 1300° to 1650°F is preferred. This can be done without jacketing, but since the scale is difficult to remove, jacketing is preferred.

POWDER METALLURGY

Powder-metallurgy techniques can probably be applied to these metals with no great difficulty. Adequate protection from the atmosphere is necessary. Powdered metals can be produced by carrying out the reduction reaction at temperatures below the melting point of the metal. Separation of the metal powder from the slag is relatively easy in the case of gadolinium because of its ferromagnetic properties below 60°F.

JOINING

Soldering, brazing, and welding techniques have not been developed for these metals.

MACHINING

Machining does not seem to be a serious problem with these metals. Cerium can be machined easily with steel tools. It can be sawed or drilled readily. It must be machined under coolant, however, for the chips and the metal itself ignite easily.

On the other hand, neodymium and gadolinium can be sawed or turned without coolant. Presumably, lanthanum and praseodymium behave more like cerium, and the elements from neodymium on up ignite less easily.

HEAT TREATMENT

Because of the allotropic transformations in some of the rare-earth metals, heat treatments might produce effects similar to those in other allotropic metals. However, to date, heat treatment of the rare-earth metals has not been extensively investigated.

CORROSION BEHAVIOR

Cerium will maintain its luster in dry air at room temperature. However, it corrodes rapidly in moist, room-temperature air. The pure metal burns in air at 320°F with evolution of much light and heat.

Corrosion resistance to mildly corrosive mediums increases relatively with increasing atomic number. Neodymium reacts less rapidly than cerium with ordinary air at room temperature. Gadolinium can be kept at room temperature in ordinary air without tarnishing. It can be heated to 1650°F in air with no more than a superficial oxide scale forming. Removal of this scale is difficult, however.

Cerium is attacked only slightly by cold water but produces a slow evolution of hydrogen from boiling water. The reactivity with water also decreases relatively with increasing atomic number.

Cerium burns brilliantly in chlorine or bromine and also combines directly with hydrogen, nitrogen, iodine, sulfur, selenium, arsenic, and antimony.

Cerium will reduce carbon monoxide and carbon dioxide, liberating carbon.

Cerium is attacked slowly by dilute hydrogen peroxide and by ammonium and potassium chloride solutions. It dissolves vigorously in the inorganic acids.

Reactions of the other rare earths in the pure form are not so well known but presumably are similar.

CONSTITUTIONAL DIAGRAMS

The following binary systems involving rare-earth metals have been studied and are reported in Haughton:¹

With La	With Ce	With Pr	With Nd
Aluminum	Silver	Aluminum	Aluminum
Gold	Aluminum	Gold	Mercury
Copper	Gold	Copper	
Mercury	Boron	Mercury	
Magnesium	Bismuth	Magnesium	
Nickel	Cobalt	Lead	
Lead	Copper	Tin	
Tin	Iron	Thallium	
Thallium	Mercury		
Zinc	Magnesium		
	Nickel		
	Lead		
	Tin		
	Thallium		
	Zinc		

¹Reference appears at end of chapter.

RARE-EARTH ALLOYS

Recently, because of interest in the high thermal-neutron cross section of gadolinium, work has been started on alloys of this metal.

Because of scarcity of the metal, alloys were made with the oxide dispersed in titanium or zirconium. They have been prepared both by arc melting and by extrusion.

A triple-arc-melted ingot of titanium, containing 4.7 wt. % Gd_2O_3 , had a Brinell hardness of 285. A 90 Ti-10 Gd_2O_3 alloy was resistant to 600°F water after 1 month. However, an 85 Zr-5 Sn-10 Gd_2O_3 alloy was rapidly attacked by 600°F.

An alloy prepared by cold compacting, evacuating, and extruding ZrH_2 plus 10 wt. % Sm_2O_3 , disintegrated in 600°F water.

Zirconium powder with 20 wt. % Gd_2O_3 and Sm_2O_3 was cold compacted in a cold can, then extruded at 1100°F with a 14:1 ratio. Resulting tensile strength was 57,000 lb/sq in. with 0.64 percent elongation as compared 120,000 lb/sq in. and 6 percent elongation for a zirconium extrusion similarly prepared.

Use of small amounts of rare-earth metals in magnesium and aluminum to augment high-temperature properties is receiving increasing attention, as are additions of rare-earth metals to ferrous materials to improve ductility and hot-working characteristics. To date, these applications use the cheaper misch metal.

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CHAPTER 1.17

Silicon Carbides

C. G. Harman

REACTOR APPLICATION

Silicon carbide has potential value as a reactor material because of its high thermal conductivity, low cross section, and refractory nature. Silicon carbide is also useful as a coating material for graphite to protect it from oxidation by air at high temperatures. Experimental fuel rods of UC or UC₂ have been coated with SiC for use in air or water.

COST AND AVAILABILITY

The availability of silicon carbide is limited only by production facilities. The basic raw materials from which it is made, silica and carbon or carbonaceous materials, are common constituents of the earth's surface.

In 1947, 33,876 tons of silicon carbide valued at \$11,451,000 were produced for abrasives alone. For all other purposes the production was 22,425 tons, the value of which was not known.

The requirements of silicon carbide for reactor application have not been fully determined, so that the availability and cost of a "reactor grade" silicon carbide is not established. Silicon carbide grains used in present experimental work generally are a high-purity product selected from commercial production.

EXTRACTION AND PURIFICATION

SYNTHESIS REACTION

The reaction between silicon and carbon to yield SiC can commence at as low as 2100°F. The formation of silicon carbide occurs more rapidly under low pressures, and there is evidence to indicate that the reaction takes place mainly in the gaseous phase.

COMMERCIAL PREPARATION

Commercial silicon carbide is prepared by heating a charge consisting of coke, silica sand, salt (NaCl), and sawdust. This is accomplished by passing an electric current through a core consisting of coke or specially prepared graphite which is surrounded by the rest of the charge. Salt is used to help volatilize impurities in the sand and coke and separate the layers of SiC after the reaction. The sawdust permits the gases, mainly CO, to escape.

After the furnace is cooled the side walls and the products are carefully removed. The outside zone consists of unreacted charge which grades into "amorphous" silicon carbide until a central zone of crystalline silicon carbide is reached. The original carbonaceous core remains as graphite.

PREPARATION FOR REACTOR USE

The applications of silicon carbide for reactor purposes are still in experimental stages, and final specifications and special procedures for its preparation for reactor use have not been established. In general, where silicon carbide grains are used, high-purity commercial silicon carbide is selected and ground to the desired grain sizes in an iron- or steel-lined ball mill with steel balls. The powdered product is leached with aqueous solutions of HCl and Na_2CO_3 to remove impurities introduced during grinding. Grinding is sometimes done in a low-ash rubber-lined ball mill with balls of steel, sintered carbides, or corundum.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants of silicon carbide are shown in Table 1.17.1 and Figs. 1.17.1 and 1.17.2.

CHEMICAL COMPOSITION OF SILICON CARBIDE

Silicon carbide is very resistant to decomposition by ordinary chemical reagents. To decompose the material without contamination, it must be first finely powdered; the carbon may then be burned off in a stream of oxygen in the presence of a strong oxidizing agent such as KNO_3 . The carbon may be collected and weighed and the analysis continued in the same manner as a clay analysis.

Some typical analyses of SiC are given in Table 1.17.2. The composition of silicon carbide depends upon the composition of the raw materials, variable factors in its production, and the electric-furnace zone in which the crystals were formed and deposited. In general, a given electric-furnace run will yield crystalline material that can be classified by color. The compositions of materials of different color are typified by the analysis in Table 1.17.3.

ALLOTROPIC TRANSFORMATIONS

The cubic form (β -SiC) is formed only below 2000°C. Near 2000°C, β -SiC is transformed to one of the hexagonal forms (α -SiC). This transformation is not known to be reversible.

CRYSTALLOGRAPHY

Only one cubic form, face-centered cubic, is known, and it is unlikely that others exist. All remaining types so far found are based on either hexagonal or rhombohedral unit cells and are designated as α -SiC.

When crystal structures were first determined, only three forms of SiC, arbitrarily designated as types I (15-layer rhombohedral), II (6-layer hexagonal), and III (4-layer hexagonal), were known. When a cubic form was discovered, it became type IV, and the 51-layer rhombohedral type next found was designated type V (Ott, 1928). Thibault (1944) more recently found two rhombohedral types, with 21 and 33 layers, respectively. He renamed the cubic form β -SiC because it has a structure corresponding to that of β -ZnS. The designation type IV (formerly cubic) he then applied to his new 21-layer structure and type VI to the 33-layer structure.

Table 1.17.1 — Physical and Chemical Constants of Silicon Carbide

Density,* gm/cm ³		
Green SiC at 30°C	3.218	
Calculated for β -SiC	3.210	
Calculated for hexagonal (6H) SiC	3.208	
Typical values at 20°C	3.10–3.30	
Melting point	Does not melt without decomposition; temperature depends on atmosphere and composition of material; values range from 2200° to 2700°C, although 2500°C is generally regarded as decomposition temperature; can be heated to 2800°C in helium; within limited range of temperature may sublime without decomposition	
Heat of formation, α -SiC, kcal/mole		
25°–1385°C	–12.3 to –12.1	
Specific heat,† α -SiC, cal/(mole)(°C)		
27°C	6.46	
327°C	10.06	
627°C	11.21	
927°C	11.98	
1227°C	12.65	
Entropy, cal/(mole)(°C)		
27°C	3.975	
327°C	9.73	
627°C	14.07	
927°C	17.41	
1227°C	20.17	
Free energy, kcal/mole		
25°C	–11.7	
627°C	–10.6	
1227°C	–9.6	
Resistivity, ohm-cm		
Temp., °C	Recrystallized, no bond	Bonded, 90% Si
20	107	107,200
800	6.5	12,500
1200	2.5	4,200
1400	1.7	1,400
Thermal expansion,‡ per °C		
0°–1700°C	$4.3\text{--}4.5 \times 10^{-6}$	
Thermal conductivity,§ cal/(sec)(cm)(°C)		
Temp., °C	Recrystallized, no bond	Bonded, SiC
500	...	0.037–0.059
600	0.040–0.049	...
800	...	0.029–0.048
1000	0.033–0.043	0.026–0.043
1300	0.027–0.040	...
Lattice parameter, A		
α -SiC	$a_0 = 3.073$ c_0 varies with number of cell layers; for 4-layer cell $c_0 = 10.053$	

*Gm/cm³ $\times 62.43 = \text{lb/cu ft}$ †Cal/(mole)(°C) $\times 1 = \text{Btu/(lb-mole)(°F)}$

‡See also Fig. 1.17.1

§Cal/(sec)(cm)(°C) $\times (2.419 \times 10^2) = \text{Btu/(hr)(ft)(°F)}$; see also Fig. 1.17.2

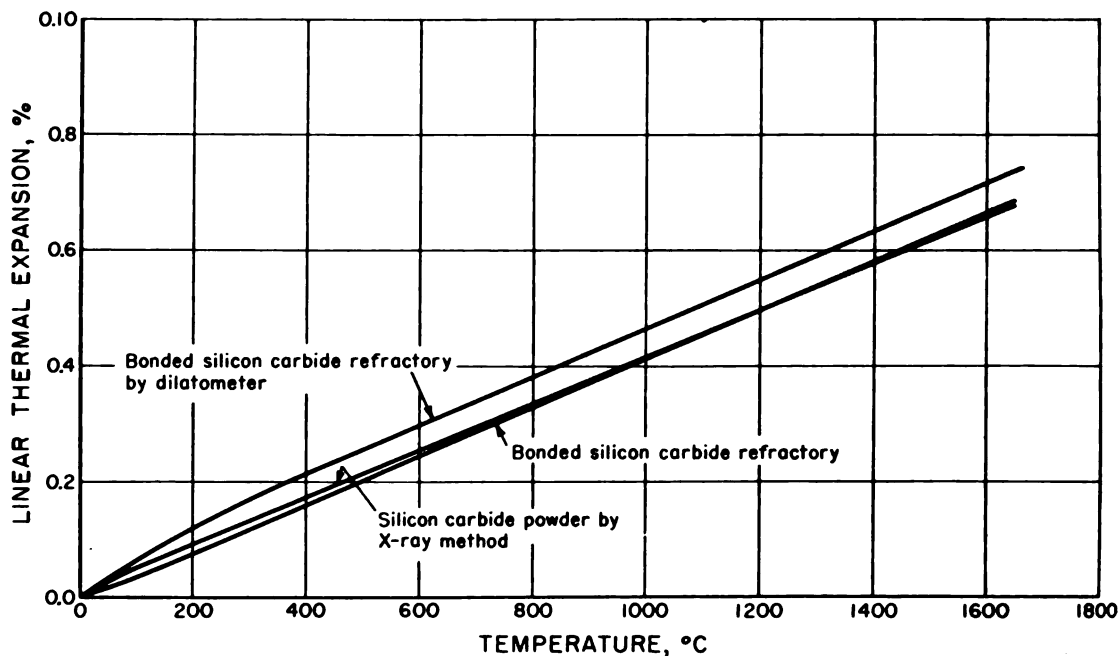


Fig. 1.17.1—Thermal Expansion of Silicon Carbide. Submitted by Battelle Memorial Institute, May 1, 1952.

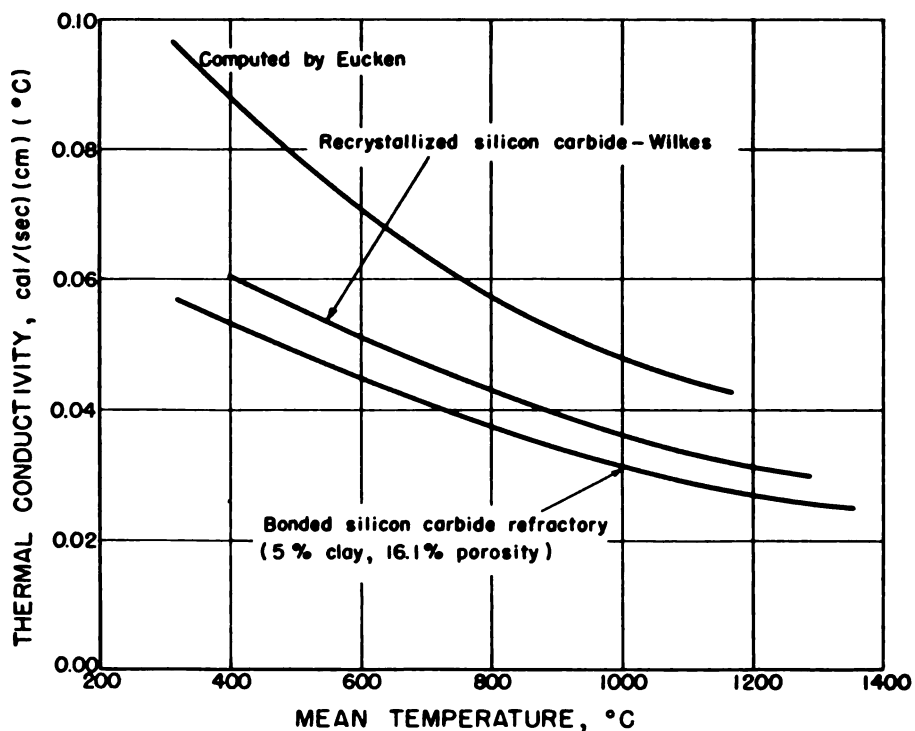


Fig. 1.17.2—Thermal Conductivity of Silicon Carbide Refractories. Prepared from Data of Eucken ("Wärmeleitfähigkeit Keramischer Feurfester Stoffe"), Wilkes ("Thermal Conductivity of Refractories") and Battelle Memorial Institute, August 1, 1952.

Table 1.17.2 — Typical Analytical Data for Silicon Carbide

Constituents	Analysis,* wt-%		
	High grade	Medium grade	Low grade
Si (combined)	~70.00	67.70	65.31
C (combined)	~29.00	28.60	27.59
Fe	0.09	0.65	0.93
Al	.55	1.40	2.02
Si (free)	.13	...	0.56
Ca	.0929

*No rare earths or other light elements are reported in the available literature as impurities in silicon carbide

Table 1.17.3 — Analyses of Some Silicon Carbides of Different Color

Constituents	Analysis,* wt-%			
	Black crystals	Green crystals	Yellow crystals	Original mixture
SiC	96.41	97.81	98.83	97.70
Al ₂ O ₃	0.31	0.18	1.17	0.31
CaO	.21	.63	0.32	.34
Fe	.22	.21	.09	.26
S	.09	.09	.34	.27
C	2.64	1.27	.29	1.02
Free SiO ₂	0.32	0.31	.28	0.35
Free Si	.08	.42	.31	.49

*No rare earths or other light elements are reported in the available literature as impurities in silicon carbide

Ramsdell recently found a crystal of SiC based on an 87-layer rhombohedral cell. Because of the very definite systematic relations evident between the 15-, 33-, 51-, and 87-layer types, Ramsdell postulated that a 69-layer rhombohedral cell also would be found. Although the 21-layer rhombohedral (IV) has no companions so far, Ramsdell believes it likely that it too may be a part of a series with still other types.

MECHANICAL PROPERTIES

Since silicon carbide shapes are made of silicon carbide grains bonded with an appropriate refractory material or by recrystallization, their mechanical properties are related to the bonding method, type of bond, and fabrication technique rather than to the inherent characteristics of silicon carbide.

HARDNESS

Silicon carbide, is a hard material with reported Knoop hardness values between 2100 and 2700, the most frequent values being near 2500.

THERMAL-SHOCK RESISTANCE

In the class of ceramic materials, silicon carbide refractories are among those most resistant to thermal shock. Standard 9-in. refractory bricks of silicon carbide of special quality have been reported to withstand 100 quenching cycles from 2500°F to room temperature in air without loss in weight due to spalling.

HIGH-TEMPERATURE STRENGTH

Table 1.17.4 illustrates the mechanical strength of conventional refractories. Silicon carbide is very rigid at high temperatures, and self-bonded brick may be heated to 3100°F under a load of 50 lb/sq in. without permanent deformation.

Table 1.17.4 — Compressive Strength of Silicon Carbide Refractories

Testing temperature, °F	Ultimate compressive strength, lb/sq in.	
	Bonded	Recrystallized
68	5790	2310
1470	5930	...
1830	8160	...
2370	2090	...
2460	1820	2440
2730	990	...

FORMING AND FABRICATION

Specific silicon carbide shapes are generally produced by one of the following four main methods:

1. By heating a carbon shape in a bed of powdered silicon carbide or in an atmosphere of silicon vapor. No limitations as to size or shape are reported in the literature for this method.
2. By pressing or ramming silicon carbide grains in the absence of any permanent bonding material and heating the resulting shape to about 3600°F to form a permanent self-bond as a result of recrystallization and crystal growth.
3. By mixing silicon carbide grain with a suitable refractory material (usually clay) which can be sintered when heated. The shapes may be formed by pressing, ramming, or slip casting.
4. Recent work indicates that dense silicon carbide may be produced by hot pressing with the aid of a small amount of additive to aid compacting.

CORROSION BEHAVIOR

Silicon carbide oxidizes slowly when heated in air. The rate of oxidation of SiC powder at temperatures between 1110 and 2190°F is illustrated in Fig. 1.17.3. The rate of oxidation is dependent upon the surface area, itself a function of such factors as porosity, grain size, and tightness of bonding. The surface of commercial silicon carbide is generally protected by a glaze of appropriate silicate material. Silicon carbide is decomposed more rapidly in the presence of water vapor than in dry air, as illustrated in Fig. 1.17.4.

Although silicon carbide is highly resistant to most common chemical reagents, it is attacked at high temperatures by many oxides and molten metals. Data regarding the reaction of SiC with molten metals are too general in nature to report here.

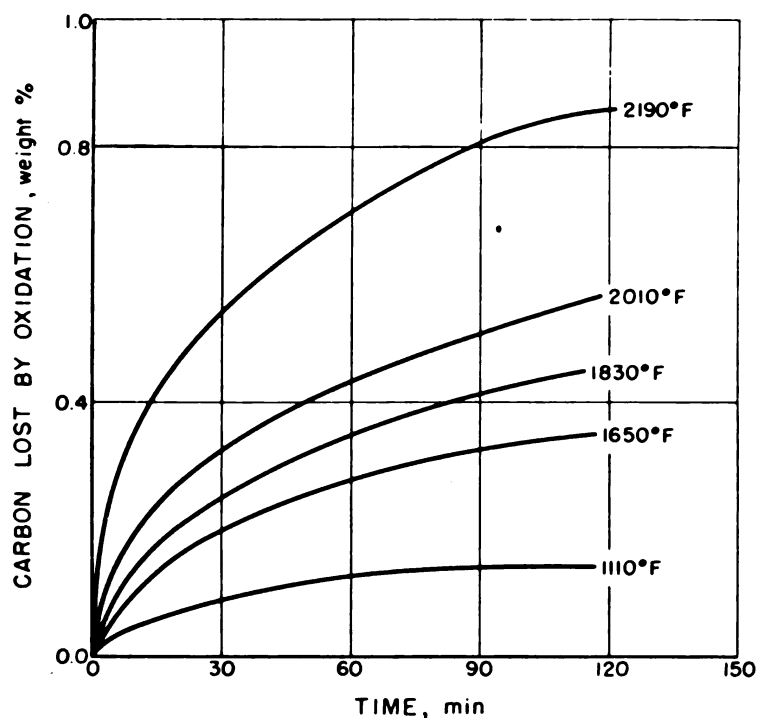


Fig. 1.17.3 — Typical Oxidation Rates for Silicon Carbide Powder in Air at Various Temperatures. Submitted by Battelle Memorial Institute, May 1, 1952.

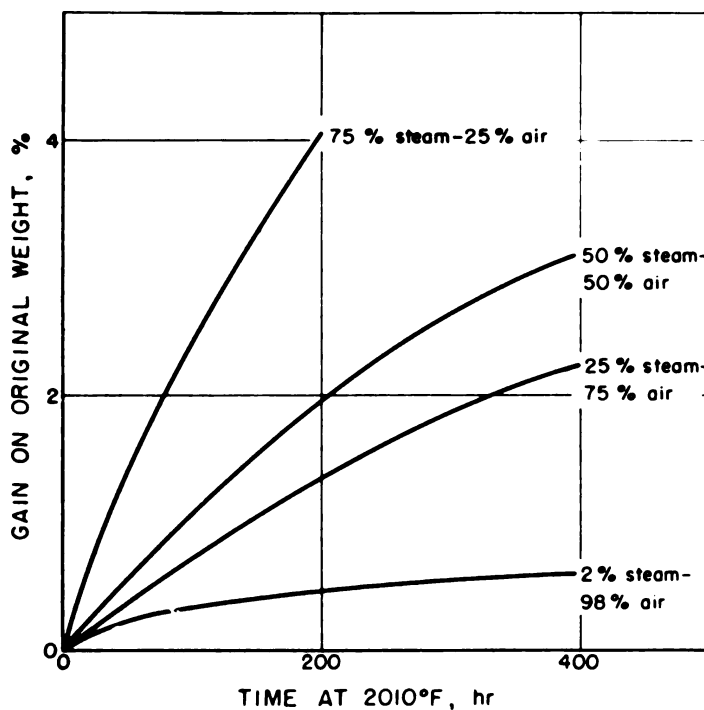


Fig. 1.17.4 — Effect of Water Vapor-Air Mixtures on the Oxidation Rate of SiC at Atmospheric Pressure and 2010°F. Submitted by Battelle Memorial Institute, May 1, 1952.

PROTECTIVE TECHNIQUES

Silicon carbide refractories are almost always protected by a coating of vitreous silicates. Inasmuch as only moderate protection has been required for industrial purposes, no extensive work on techniques for the protection of silicon carbide is available for reactor applications.

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CHAPTER 1.18

Stainless Steels

Erwin Eichen, J. H. Jackson, W. K. Boyd, and R. S. Peoples

INTRODUCTION

Because of their strength at elevated temperatures and their generally good corrosion resistance stainless steels are important for reactors. They are used not only for piping, heat exchangers, and other auxiliary reactor components, but also as the basic material for the fabrication of fuel elements in several reactors.

Stainless steels can be supplied in either cast or wrought form. Table 1.18.1 lists chemical compositions of various cast alloys, and Table 1.18.2 lists compositions of

Table 1.18.1 — Composition of Cast Stainless Steels

ACI and ASTM designation*	Composition, %							
	C	Mn (max)	Si (max)	P (max)	S (max)	Cr	Ni	Other
BC	0.50(max)	1.00	2.00	0.04	0.04	26-30	4.0(max)	†
BD	.50(max)	1.50	2.00	.04	.04	26-30	4-7	†
BE	.20-0.50	2.00	2.00	.04	.04	26-30	8-11	†
BF	.20-0.40	2.00	2.00	.04	.04	18-23	8-12	†
HH (Type I)	.20-0.50	2.00	2.00	.04	.04	24-28	11-14	N ₂ = 0.20(max)†
HH (Type II)	.20-0.50	2.00	2.00	.04	.04	24-28	11-14	N ₂ = 0.20(max)†
HI	.20-0.50	2.00	2.00	.04	.04	26-30	14-18	†
HK	.20-0.60	2.00	3.00	.04	.04	24-28	18-22	†
HL	.20-0.60	2.00	3.00	.04	.04	28-32	18-22	†
HT	.35-0.75	2.00	2.50	.04	.04	13-17	33-37	†
HU	.35-0.75	2.00	2.50	.04	.04	17-21	37-41	†
HW	.35-.75	2.00	2.50	.04	.04	10-14	58-62	†
HX	.35-.75	2.00	2.50	.04	.04	15-19	64-68	†
CA-15	.15(max)	1.00	1.50	.04	.04	11.5-14	1.0(max)	†
CA-40	.20-.40	1.00	1.50	.04	.04	11.5-14	1.0(max)	†
CB-30	.30(max)	1.00	1.00	.04	.04	18-22	2.0(max)	...
CC-50	.50(max)	1.00	1.00	.04	.04	26-30	4.0(max)	...
CE-30	.30(max)	1.50	2.00	.04	.04	26-30	8-11	...
CF-8	.08(max)	1.50	2.00	.04	.04	18-21	8-11	...
CF-8M	.08(max)	1.50	1.50	.04	.04	18-21	9-21	Mo = 2.0-3.0
CF-8C	.08(max)	1.50	2.00	.04	.04	18-21	9-12	Co 8 × C(min), 1.0 Nb(max) or Nb-Ta 10 × C(min), 1.35(max)
CF-12M	.12(max)	1.50	1.50	.04	.04	18-21	9-21	Mo = 2.0-3.0
CF-16F	.16(max)	1.50	2.00	.17	.04	18-21	9.12	Mo = 1.5(max), Se = 2.0-3.0
CF-20	.20(max)	1.50	2.00	.04	.04	18-21	8-11	...
CH-20	.20(max)	1.50	2.00	.04	.04	22-26	12-15	...
CK-20	.20(max)	1.50	2.00	.04	.04	23-27	19-22	...

*Alloys intended primarily for heat-resistant applications have "H" as the first letter of the designation, whereas alloys for corrosion-resistant applications have "C" as the first letter

†Molybdenum, 0.50 max (not added intentionally)

Table 1.18.2—The Composition of Wrought Stainless Steels

Class and composition limits	AISI and ASTM designation	Composition, %							
		C	Mn (max)	Si (max)	P (max)	S (max)	Cr	Ni	Other
Austenitic, Nonhardenable, nonmagnetic, C = 0.25(max), Cr = 16.0–26.0, Ni = 6.0–22.0	301	0.08(min)–.20(max)	2.0	1.0	0.04	0.04	16.0–18.0	6.0–8.0	
	302	.08(min)–.20(max)	2.0	1.0	.04	.04	17.0–19.0	8.0–10.0	
	302B	.08(min)–.20(max)	2.0	2.0–3.0	.04	.04	17.0–19.0	8.0–10.0	
	303	.20(max)	2.0	1.0	17.0–19.0	8.0–10.0	*
	304	.08(max)	2.0	2.0	1.0	.04	18.0–20.0	8.0–10.0	
	305	.08(max)	2.0	2.0	0.04	.04	17.0–19.0	10.0–13.0	
	308	.08(max)	2.0	1.0	.04	.04	19.0–21.0	10.0–12.0	
	309†	.20(max)	2.0	1.0	.04	.04	22.0–24.0	12.0–19.0	
	310	.25(max)	2.0	1.5	.04	.04	24.0–26.0	19.0–22.0	
	316	.10(max)	2.0	1.0	.04	.04	16.0–18.0	10.0–14.0	Mo = 2.00/3.00
	317	.10(max)	2.0	1.0	.04	.04	17.5–20.0	10.0–14.0	Mo = 3.0/4.0
	318	.08(max)	2.5	1.0	.04	.04	17.0–19.0	13.0–15.0	Mo = 2.0/2.75, Nb = 10 × C(min)
	321	.10(max)	2.0	1.0	.04	.04	17.0–19.0	8.0–11.0	Ti‡ = 5 × C(min)
	330	.10(max)	2.0	1.0	.04	.04	14.0–16.0	33.0–36.0	
	347†	.10(max)	2.0	1.0	.04	.04	17.0–19.0	9.0–12.0	Nb = 10 × C(min)
Martensitic, Hardenable, magnetic, C = 0.15–1.20, Cr = 4.0–18.0, Ni = 2.50(max)	403	.15(max)	1.0	1.0	0.04	0.04	11.5–13.0		Turbine quality
	410	.15(max)	1.0	1.0	.04	.04	11.5–13.5		
	414	.15(max)	1.0	1.0	.04	.04	11.5–13.5	1.25–2.50	
	416	.15(max)	1.0	1.0	.04	.04	12.0–14.0		*
	418	.15(max)	1.0	1.0	.04	.04	12.0–14.0	0.50	W = 2.50/3.50
	420	.15(min)	1.0	1.0	.04	.04	12.0–14.0		*
	420F	.15(min)	1.0	1.0	12.0–14.0		
	431	.20(max)	1.0	1.0	.04	.04	15.0–17.0	1.25–2.50	
	440A	.60–0.75	1.0	1.0	.04	.04	16.0–18.0		
	440B	.75–0.95	1.0	1.0	.04	.04	16.0–18.0		
	440C	.95–1.20	1.0	1.0	.04	.04	16.0–18.0		
	440F	.05–1.20	1.0	1.0	16.0–18.0		*
	501	.10(min)	1.0	1.0	.04	.04	4.0–6.0		
	502	.10(max)	1.0	1.0	.04	.04	4.0–6.0		
Ferritic, Nonhardenable, magnetic, C = 0.35(max), Cr = 14.0–28.0, Ni = None	405	0.08(max)	1.0	1.0	0.04	0.04	11.5–13.5		Al = 0.1–0.3†
	406	.15(max)	1.0	1.0	.04	.04	12.0–14.0		Al = 3.5–4.5
	430	.12(max)	1.0	1.0	.04	.04	14.0–18.0		
	430F	.12(max)	1.0	1.0	.04	.04	14.0–18.0		*
	442	.35(max)	1.0	1.0	.04	.04	18.0–23.0		
	443	.20(max)	1.0	1.0	.04	.04	18.0–23.0		Cu = 0.90–1.25
	446	.35(max)	1.0	1.0	.04	.04	23.0–27.0		

*Free-machining stainless steel, P, S, or Se(min) = 0.07%

†Made in a stabilized grade by addition of Nb = 10 × C(min)

‡Made in a free-machining grade by addition of Se = 0.15–0.35 and P = 0.11–0.17

§Stabilization with titanium is undesirable from the standpoint of increasing the nuclear cross section of the alloys

¶Also available containing 0.5 molybdenum for high-temperature use

wrought alloys. Because of the inherent differences in the strength characteristics and corrosion resistance of these two types of materials, they will be considered separately.

Wrought stainless steels are further subdivided into three categories according to their microstructure, martensitic, ferritic, and austenitic, as shown in Table 1.18.2. If the alloy can be hardened by heat treatment, i.e., austenitizing and quenching, it belongs to the martensitic group; if its microstructure is ferrite at all temperatures, the alloy is classified as ferritic; and if the microstructure is austenite at all temperatures, the alloy is classified as austenitic.

There is a considerable amount of information available in the open literature on stainless steels, and to include all this information is beyond the scope of this handbook. Wherever possible, therefore, a specific property will be listed below for a whole group of alloys rather than for each individual alloy in the group. Some indication will be given, however as to how the property varies throughout the composition range of the group of alloys.

ABUNDANCE AND AVAILABILITY

AVAILABILITY

The availability of stainless steels is dependent on their component elements. The following discussion is based on the alloy outlook for the early part of 1952.

CHROMIUM

Chromium is the major alloying constituent in the majority of stainless steels. At present, there is enough chromium available for all needs, and barring a considerable increase in chromium requirements in the near future, there should be no shortage.

NICKEL

Nickel is used in large quantities in austenitic alloys. At present, there is a definite shortage of nickel. As long as there is a need for high-temperature alloys of the Inconel or Nimonic types for jet-engine and other military uses, this situation will probably not improve.

MOLYBDENUM

Small percentages of molybdenum are used in certain stainless steels. Unless there is a very large increase in the amount of pure molybdenum used for high-temperature applications, there should be no long-range shortage of molybdenum. Meanwhile, however, there is a temporary shortage of molybdenums brought about by shortage of production facilities and government stockpiling.

NIOBIUM (*Columbium*)

Niobium is used as a stabilizer in austenitic stainless steels and is also used in some of the "softer alloys." In the stainless steels, it prevents intergranular corrosion attack in these alloys during heating in the range from 800° to 1600°F, especially at 1000° to 1100°F. At present, niobium is a very critical element being used in large quantities in high-temperature "superalloys." As long as there is a large military need for this type of alloy, there will be no improvement in the availability of niobium. To conserve this critical material, tantalum is being used in conjunction with niobium as a stabilizer, but the outlook for this element is still critical. The use of titanium as a stabilizer to replace niobium is discussed in the following paragraph.

TITANIUM

Titanium may be used as a substitute for niobium in the stabilization of austenitic stainless steel. The outlook for the availability of titanium for this purpose is good, and no shortage of this material is predicted for the foreseeable future. However, the use of titanium for the stabilization of stainless steels presents problems, and titanium has not been accepted as equivalent to niobium, especially when welding is introduced.

The substitution of either tantalum or titanium for niobium is undesirable from the standpoint of increasing the nuclear cross section of the alloys. Tantalum is particularly undesirable because of the formation of an unstable, long-lived isotope during irradiation.

COST

The price of stainless steel is dependent on the type of alloy required, and the price fluctuates from time to time. In April 1952, the base price of stainless sheet ranged from \$0.365/lb for Type 410 to \$0.57/lb for Type 316. At the same time, the base price of cold-rolled strip was \$0.305 and \$0.59/lb for Types 410 and 316, respectively. Extras such as small sizes, special shapes and finishes, and small amounts raise the base price.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants of various stainless steels are given in Table 1.18.3.

THERMAL-NEUTRON ABSORPTION CROSS SECTION

The thermal cross section of each stainless steel is dependent on the composition of the alloy. If the amount of each element in the steel and its thermal cross section are known, the thermal cross section of the alloy may be computed using the "method of mixtures." A list of the thermal-neutron-absorption cross sections of the elements is given in the Appendix of this volume.

CRYSTALLOGRAPHY

The crystal structure of a stainless steel is dependent upon its composition and prior thermal treatment. Average lattice constants of the three principal constituents, ferrite, austenite, and fast-formed (untempered) martensite are 2.86, 3.56, and 2.85 Å, respectively.

MECHANICAL PROPERTIES

The strength and ductility of a stainless steel depend not only on the composition of the steel, but also on its prior history. Therefore, in reporting room-temperature strength and ductility values, it is very important to note the condition of the material tested. A considerable amount of data on the mechanical properties of stainless steel is available in the literature. In practically all instances, the value of any specific mechanical property reported by more than one source varies for material in the same condition, and therefore, the mechanical properties listed here represent average values. In cases where there were large discrepancies among reported values, an attempt was made to evaluate the testing methods to arrive at an average value of the best data. Thus, representative values rather than specification values are reported here.

Table 1.18.3 — Physical and Chemical Constants of Various Stainless Steels

Constant	Austenitic			Martensitic			Ferritic		Range of all types of stainless steel
	Type	Type	Type	Type	Type	Type	Type	Type	
	310	316	321	347	410	416	430	446	
Density, * gm/cm ³	7.92	7.92	7.92	7.98	7.75	7.73	7.70	7.60	Cast 7.58–7.75 Wrought 7.60–7.98
Melting range, °C	1370–1425	1370–1400	1400–1425	...	1480–1510	1480–1510	1450–1510	1450–1480	1370–1510
Electrical resistivity, μ ohm-cm	20°C 400°C 800°C	76	72	72 100 121	57 88 111(700°)	57	60	67 98 119	45–79 88–104.5 115–121
Coefficient of linear thermal expansion, 10 ⁻⁴ /°C	100°C 600°C 1000°C	16.0 17.2 19.7	16.5 18.0 20.0	16.5 18.0 20.0	10.2 11.2 13.2	10.1 11.5(500°) 12.4(787°)	10.0 10.5 12.0	8.8 10.0 11.2	8.8–17.0 10.0–18.0 11.2–20.0
Thermal conductivity, † cal/(cm)(sec)(°C)	100°C 500°C	0.032 .040	0.035 .050	0.037 .052	0.037 .052	0.060 .065	0.057 .062	0.050 .058	0.032–0.087 .040–0.080
Specific heat, ‡ cal/(cm)(°C)			0.12		0.11		0.11		...
Magnetism			Nonmagnetic‡		Ferromagnetic		Ferromagnetic		...

*Gm/cm³ × 62.43 = lb/cu ft†Cal/(sec)(cm)(°C) × (2.419 × 10⁵) = Btu/(hr)(ft)(°F)

‡Cal/(gm)(°C) × 1 = Btu/(lb)(°F)

§Can be slightly magnetic after cold working

CAST STAINLESS STEELS

ROOM-TEMPERATURE PROPERTIES

Table 1.18.4 lists room-temperature mechanical properties of cast stainless steel. Where possible, values are given for the as-cast and heat-treated conditions. The heat treatment specified for each alloy is the one which is most usually given to the alloy.

Table 1.18.4—Typical Room-temperature Mechanical Properties of Cast Stainless Steels

ASTM and ACI designation	Tensile strength, 10 ³ lb/sq in.		Yield strength (0.2% offset), 10 ³ lb/sq in.		Elongation in 2 in., %		Brinell hardness,		Charpy impact strength, ft-lb	
	As cast	Heat treated	As cast	Heat treated	As cast	Heat treated	As cast	Heat treated	As cast	Heat treated
HC	70.0	...	65.0	...	2	...	190
HD	85.0	...	48.0	...	16	...	190
HE	87.0	85.0°	45.0	65.0°	10	3°	200	270°	10	...
HF	85.0	100.0	45.0	50.0°	35	25°	165	190°
HH (Type 1)	80.0	86.0°	50.0	55.0°	25	11°	185	200°
HH (Type 2)	85.0	92.0°	45.0	40.0°	15	8°	180	200°	15	4°
HI	80.0	90.0°	55.0	70.0°	8	6°	180	200°
HK	75.0	85.0°	50.0	50.0°	17	10°	170	190
HL	86.0	...	53.0	...	19	...	192
HT	70.0	75.0‡	40.0	45.0‡	10	5‡	180	200‡	4	5‡
HU	70.0	73.0‡	40.0	43.0‡	9	5‡	170	190‡	4	5‡
HW	68.0	84.0°	36.0	52.0°	8	6°	185	205°
HX	55.6	82.0‡	25.0	50.0‡	9	9‡	170	185‡
CA-15	...	100.0§	...	75.0§	...	30§	...	185§	...	35§
	...	135.0¶	...	115.0¶
	...	95.0†	...	70.0**	...	17†	...	260†	...	10†
CA-40	...	110.0††	...	67.0††	...	18††	...	212††
	...	135.0‡‡	...	120.0‡‡	...	12‡‡	...	269‡‡
CB-30	...	75.0§§	...	50.0§§	...	10§§	...	170§§	...	2§§
CC-50	70.0***	97.0§§.¶¶	65.0***	65.0§§.¶¶	2***	18§§.¶¶	212***	210§§.¶¶	2***	...
	95.0†††	...	60.0†††	...	15†††	...	193	...	45†††	...
CE-30	95.0	97.0‡‡‡	60.0	63.0‡‡‡	15	18‡‡‡	170	170‡‡‡
CF-8	78.0	75.0‡‡‡	43.0	35.0‡‡‡	45	55‡‡‡	150	140‡‡‡	...	75‡‡‡
CF-8M	...	88.0‡‡‡	...	45.0‡‡‡	...	50‡‡‡	...	156‡‡‡	...	70‡‡‡
CF-8C	...	85.0‡‡‡	...	44.0‡‡‡	...	45‡‡‡	...	149‡‡‡	...	30‡‡‡
CF-12M	...	88.0§§§	...	45.0§§§	...	50§§§	...	170§§§
CF-16F	...	80.0‡‡‡	...	42.0‡‡‡	...	45‡‡‡	...	150‡‡‡
CF-20	...	83.0§§§	...	42.0§§§	...	55§§§	...	163§§§	...	60§§§
CH-20	84.0	88.0¶¶¶	48.0	50.0¶¶¶	24	38¶¶¶	196	180¶¶¶	...	30¶¶¶
CK-20	65.0	76.0****	35.0	38.0****	22	21****	196	180****	...	50****

Heat treatments:

* 24 hr at 1400°F, furnace-cooled

† 48 hr at 1600°F, air-cooled

‡ 48 hr at 1800°F, air-cooled

§ Air-cooled from 1800°F, then
drawn at 1400°–1500°F¶ Air-cooled from 1800°F, drawn
at 1100°F** Oil-quenched from 1300°F,
drawn at 1200°F†† Air-cooled from 1800°F, drawn
at 1400°F‡‡ Air-cooled from 1800°F, drawn
at 1125°F§§ Heated at 1450°–1500°F, furnace-
cooled to 1100°F, air-cooled

¶¶ Air-cooled from 1900°F

*** Ni content below 1%

††† Ni above 2% with 0.15% N

‡‡‡ Water-quenched from 1950°–2050°F

§§§ Heated to 2000°F or higher, water-
quenched¶¶¶ Heated to 1950°–2050°F or higher,
water-quenched

**** Heated to 2100°F, water-quenched

ELEVATED-TEMPERATURE PROPERTIES

Elevated-temperature properties are given only for cast heat-resistant steels; these materials, which are used primarily for their elevated-temperature strength, are designated by their first letter "H." Those alloys designated by their first letter as "C" are used primarily where corrosion resistance is desired. In general, it can be said that the elevated-temperature strength of "H"-type (heat-resistant) alloys is greater than that of the "C"-type (corrosion-resistant) alloys.

Table 1.18.5 lists short-time elevated temperature tensile properties of the heat-resistant cast steels. Tables 1.18.6 and 1.18.7 list creep strength and stress-rupture properties of these alloys.

Table 1.18.5—Typical Short-time Elevated-temperature Tensile Properties of Cast Stainless Steels

Property	Temperature, °F	ACI designation										
		HC*	HD	HF	HH (Type I)	HH (Type II)	HK	HL	HT	HU	HW	HX
Tensile strength, 10 ³ lb/sq in.	1000	53.5	48.0
	1200	57.0	42.4	45.0
	1400	10.5	36.0	35.0	33.0	35.0	...	50.0	35.0	40.0	32.0†	42.0
	1600	5.1	23.0	22.0	18.5	22.0	23.0	30.4	18.8	19.6	19.0	...
	1800	2.5	15.0	...	9.0	11.0	...	18.7	11.0	10.0	10.0	10.7
	2000	6.0
Yield strength (0.2% offset), 10 ³ lb/sq in.	1000	33.0	21.0
	1200	28.0	20.0
	1400	8.7	...	17.0	18.0	26.0	...	23.0	19.5
	1600	3.8	...	13.5	14.0	15.0	...	15.0	17.5
	1800	2.1	...	6.3	7.0	8.0	6.2	8.0	6.9
	2000
Elongation in 2 in., %	1000	6	9
	1200	16	5	8
	1400	65	14	20	18	12	10	11
	1600	94	18	22	30	16	21	...	26	20	...	48
	1800	110	40	...	45	30	28	28	40	40
	2000

*Extrapolated values

†2.8% nickel, 0.15% nitrogen

Table 1.18.6—Typical Creep Strength of Cast Stainless Steels

Temperature, °F	Limiting creep strength (0.0001 %/hr), lb/sq in. (ACI designations)												
	HC*	HD	HE	HF	HH (Type I)	HH (Type II)	HI	HK	HL	HT	HV	HW	HX
1000
1200	13,000
1400	11,300	3,500	3,500	6,000	3,000	7,000	6,600	6,800	7,000	8,000	8,500	6,000	6,400
1600	750	1,900	2,000	3,200	1,700	4,000	3,600	4,200	4,300	4,500	5,000	3,000	3,200
1800	360	900	1,000	...	1,100	2,100	1,900	2,700	...	2,000	2,200	1,400	1,600
2000	300	800	800	1,000	...	500	600	500†	600
2150	150	200	...	150

*2.8% nickel, 0.15% nitrogen

†Extrapolated

Table 1.18.7—Stress-rupture Properties of Cast Stainless Steels

Stress to rupture, lb/sq in. (ACI designations)														
Time, hr	Temper- ature, °F	HC	HD	HE	HF	HH (Type I)	HH (Type II)	HI	HK	HL	HT	HU	HW	HX
10	1000
	1200	37,000
	1400	5,100	20,000	...	20,000	...	23,000	16,000	18,000
	1600	10,000	...	10,000	...	11,000	...	11,000	...	8,300	10,000
	1800	1,100	4,700	6,000	...	6,500	...	5,800	...	4,300	5,400
	2000	2,000	2,500
100	1000
	1200	30,000	...	35,000
	1400	3,300	10,000	11,000	14,000	14,000	14,000	13,000	14,500	15,000	16,000	15,000	10,000	13,000
	1600	1,700	5,000	5,300	6,000	6,400	7,500	7,500	7,000	9,800	8,000	8,000	8,000	6,700
	1800	1,000	2,500	2,500	...	3,100	4,000	4,100	4,500	5,800	4,500	4,500	3,000	3,500
	2000	1,500	1,800	1,000	2,500	...	2,500	1,700
1000	1000
	1200	17,000	...	22,000
	1400	2,300	8,000	6,500	10,000	8,500	9,000	...	12,500	...	7,000	...
	1600	1,300	3,000	3,800	4,700	4,800	5,000	...	7,000	6,000	4,500	4,000
	1800	620	2,100	2,500	2,000	3,000	...	3,700	2,000	2,000	2,300
	2000	1,200	1,250	1,500	500

WROUGHT STAINLESS STEELS**ROOM-TEMPERATURE PROPERTIES**

Table 1.18.8 lists room-temperature properties of wrought stainless steels. Austenitic- and ferritic-type alloys can be strengthened by cold working. In fact, an alloy such as Type 302 can have its tensile strength increased from 80,000 to 200,000 or 250,000 lb/sq in. by cold work; therefore, the actual mechanical properties of these steels at room temperature can be controlled over a wide range by regulating the amount of cold work which is done on the alloy. Examples of the increased strength obtained by cold working Types 302 and 303 stainless steel are shown in Table 1.18.9.

ELEVATED-TEMPERATURE PROPERTIES

The elevated-temperature strength of metals and alloys is measured by two types of tests. The first is a short-time tensile test similar, except for testing temperature, to that used to determine the room-temperature properties of alloys. The second type is a long-time test; creep and stress-rupture tests fall into this category. Creep tests are conducted by applying a fixed load to a specimen at the temperature of interest. The deformation of the specimen is measured at given time intervals. Creep strength is reported usually as the load per unit area necessary to cause a specified deformation rate, usually 0.0001 percent/hr (often stated erroneously as 1 percent in 10,000 hours).

Stress-rupture or creep-rupture tests are very similar to creep tests except that testing times are shorter and applied stresses are higher. In the case of stress-rupture testing, the time necessary for a fixed load to cause a specimen to fracture is reported.

Tables 1.18.10 through 1.18.27 give average representative values for short-time elevated-temperature tensile properties of different types of stainless steels. It will be noted from this table that the strength of the straight chromium steels at temperatures greater than 1100°F is poor compared with the strength of the nickel-chromium steels.

Figures 1.18.1 through 1.18.6 are plots of creep strength versus temperature and of rupture strength versus temperature for various stainless steels. These are average values representative of the creep and rupture strength of these alloys. Here again, it is noted that the creep and rupture properties of the austenitic alloys are superior to those of the straight chromium type.

Table 1.18.8—Typical Room-temperature Physical Properties of Wrought Stainless Steels

AISI and ASTM designation, type number	Tensile strength, 10 ³ lb/sq in.		Yield strength (0.2% offset), 10 ³ lb/sq in.		Elongation in 2 in., %		Reduction of area, %	Mod of impact, ft-lb	Rockwell hardness		Brinell hardness		Modulus of elasticity, [†] 10 ³ lb/sq in.	Shear modulus, 10 ³ lb/sq in.	Poisson's ratio	Endurance limit (10 ⁷ cycles), 10 ³ lb/sq in.
	Annealed*	Hardened	Annealed	Hardened	Annealed	Hardened			Annealed	Hardened	Annealed	Hardened				
301	100.0	...	40.0	...	50.0	...	80.0	95.0	B90	...	180	...	29.0
303	80.0	...	30.0	...	50.0	...	80.0	85.0	B90	...	180	...	29.0	11.2	0.297	33
302B	90.0	...	35.0	...	40.0	...	80.0	80.0	B90	...	180	...	29.0
308	78.0	...	30.0	...	40.0	...	80.0	85.0	B90	...	180	...	29.0	34.5
304	80.0	...	30.0	...	50.0	...	80.0	80.0	B90	...	180	...	29.0	35
305	78.0	...	25.0	...	50.0	...	80.0	85.0	B90	...	180	...	29.0
308	80.0	...	30.0	...	40.0	...	80.0	70.0	B95	...	200	...	29.0
309	80.0	...	30.0	...	40.0	...	80.0	80.0	B95	...	200	...	29.0
310	80.0	...	35.0	...	40.0	...	80.0	80.0	B90	...	180	...	30.0	11.2	.283	33
316	78.0	...	30.0	...	40.0	...	80.0	70.0	B95	...	200	...	29.0
317	78.0	...	30.0	...	40.0	...	80.0	70.0	B95	...	200	...	29.0
318	75.0	...	30.0	...	40.0	...	80.0	70.0	B95	...	200	...	29.0
321	85.0	...	30.0	...	40.0	...	80.0	80.0	B95	...	200	...	29.0	11.2	.268	...
330	85.2	...	40.0	...	46.0	...	72.0	98.0
347	85.0	...	35.0	...	40.0	...	80.0	80.0	B95	...	200	...	29.0	11.4	.284	...
403	85.0	200.0	35.0	165.0	20.0	2.0	50.0	85.0	B95	C45	200	400	30.1	12.5	.268	...
406	80.0	...	32.0	...	20.0	...	50.0	35.0	B90	...	180	...	29.0
410	85.0	200.0	35.0	165.0	20.0	2.0	50.0	85.0	B95	C45	200	400	29.0	12.5	.268	45
414	100.0	220.0	65.0	175.0	15.0	2.0	50.0	80.0	C30	C45	280	440	29.0
416	95.0	200.0	60.0	115.0	15.0	15.0	40.0	...	B90	C30	180	280	29.0
418	78.0	200.0	40.0	180.0	20.0	10.0	50.0	80.0	B96	C40	212	400	29.0
420	90.0	270.0	60.0	220.0	15.0	3.0	40.0	...	B100	C55	240	550	29.0
430F	95.0	245.0	60.0	175.0	15.0	5.0	40.0	...	B100	C50	240	500	29.0
430	85.0	...	35.0	...	20.0	...	40.0	...	B95	...	200	...	29.0
430F	85.0	...	35.0	...	15.0	...	40.0	29.0
431	105.0	220.0	90.0	185.0	20.0	10.0	80.0	70.0	C28	C45	270	440	28.0	45
440A	95.0	275.0	55.0	240.0	20.0	2.0	40.0	...	B100	C55	240	555	31.8	13.5	.264	...
440C	100.0	285.0	60.0	275.0	8.0	1.0	35.0	...	B105	C58	280	800	31.8	13.5	.264	...
440F	100.0	285.0	60.0	275.0	8.0	1.0	35.0	...	B105	C58	280	800	31.8	13.5	.264	...
442	80.0	...	45.0	...	20.0	...	40.0	...	B95	...	200	...	29.0	47
446	75.0	...	45.0	...	20.0	...	40.0	...	B95	...	200	...	29.7	11.9	.283	44
501	60.0	220.0	25.0	175.0	30.0	14.9	70.0	85.0	B85	C40	180	388	29.0
502	60.0	220.0	25.0	175.0	30.0	14.9	70.0	85.0	B85	C40	180	388	29.0

*The strength properties of annealed austenitic stainless steels can be increased greatly by cold work. Typical examples are shown in Table 1.18.9

†Static determination

Table 1.18.9 — Typical Properties of Cold-worked, Austenitic, Stainless Steel

Type	Condition	Tensile strength, lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Elongation in 2 in., %	Brinell hardness number
302	Water-quenched	86,500	38,100	64.0	156
	Cold-reduced 11%	106,200	84,500	44.0	...
	Cold-reduced 12.3%	105,700	80,200	43.0	229
	Cold-reduced 19.3%	116,000	99,800	31.5	...
	Cold-reduced 21%	119,800	104,300	24.5	217
303	Water-quenched	98,500	38,000	58.5	163
	Cold-reduced 9%	108,500	71,500	46.0	255
	Cold-reduced 16%	121,000	92,200	31.0	...
	Cold-reduced 26%	132,500	114,000	22.0	293
	Cold-reduced 30%	151,800	141,000	10.0	...

Table 1.18.10 — Typical Short-time Elevated-temperature Tensile Properties of Type 302 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	79.2	26.0	55.0	77.0	27.3	10.4	0.307
500	75.8	22.7	51.0	72.5	26.0	9.8	.313
800	73.0	19.8	51.0	71.0	24.2	9.0	.319
900	23.6	8.8	.320
1000	65.6	17.1	45.0	65.0	23.0	8.6	.322
1100	22.3	8.4	.323
1200	52.0	15.5	37.0	44.0	21.8	8.2	.325
1300	21.2	7.9	.327
1400	31.8	14.9	21.0	64.0	20.6	7.7	.332
1500	20.0	7.5	.336
1600	15.7	64.0

*Static determination

Table 1.18.11 — Typical Short-time Elevated-temperature Tensile Properties of Type 303 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	80.0	...	46.0	60.0
500	74.5	...	40.0	55.0
800	67.5	...	35.0	52.0
900
1000	61.0	...	34.0	54.0
1100
1200	46.0	...	30.0	53.0
1300
1400	30.0	...	20.0	44.0
1500
1600	20.0	...	10.0	42.0

*Static determination

**Table 1.18.12 — Typical Short-time Elevated-temperature
Tensile Properties of Type 304 Stainless Steel**

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	67.0	38.0	50.5	72.0	26.5
500	65.0	34.0	47.0	68.5	24.5
800	62.5	21.5	47.0	62.9	21.0
900	56.9	19.5	45.0	67.0
1000	55.0	18.5	43.5	65.1	19.2
1100	51.0	...	37.0
1200	45.2	16.5	36.0	58.6	18.5
1300	34.3	15.0	35.5	50.5
1400	28.5	12.5	31.0	45.1	17.2
1500	19.4	16.0
1600	17.5	10.0	...	28.5	15.2

*Static determination

**Table 1.18.13 — Typical Short-time Elevated-temperature
Tensile Properties of Type 309 Stainless Steel**

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	81.5	37.0	50.0	77.0
500	77.0	32.0	47.0	75.0
800	71.5	27.0	45.0	58.6	23.1
900	69.1	25.5	43.0
1000	64.0	24.0	34.0	56.1	22.6
1100	59.0	23.0	35.0	58.0
1200	53.5	22.3	29.8	42.0	21.8
1300	44.2	21.5	37.0	...	21.2
1400	37.0	21.0	30.0	42.0
1500	26.6	19.0	28.0	44.0	19.8
1600	20.2	18.0	25.0	...	19.2

*Static determination

**Table 1.18.14 — Typical Short-time Elevated-temperature
Tensile Properties of Type 309 Stainless Steel**

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	87.5	35.0	47.0	73.0	27.5	10.6	0.299
500	83.5	32.0	39.0	71.0	26.2	10.0	.305
800	82.5	25.0	39.0	69.0	24.2	9.1	.314
900	79.5	21.0	39.0	66.0	23.6	8.8	.317
1000	73.0	22.0	36.0	57.0	23.0	8.5	.320
1100	63.5	...	33.5	56.0	22.4	8.2	.324
1200	57.2	21.0	33.0	43.0	21.8	7.9	.326
1300	45.3	20.5	30.0	44.0	21.2	7.6	.330
1400	36.7	18.0	...	42.0	20.5	7.2	.333
1500	25.4	16.5	...	45.0	19.8	6.9	.336
1600	18.6	43.0	19.2	6.6	.339

*Static determination

Table 1.18.15—Typical Short-time Elevated-temperature
Tensile Properties of Type 314 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300
500
800	82.3	40.0	28.0
900
1000	78.4	33.5	33.4	52.0
1100	71.5	32.5	37.5	35.0
1200	61.2	30.0	36.5	37.5
1300
1400	38.3	20.0	54.0
1500	25.0	15.0	55.0	50.5
1600	22.3	13.0	58.0

Table 1.18.16—Typical Short-time Elevated-temperature
Tensile Properties of Type 316 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	76.0	31.0	53.0	75.0
500	73.5	27.0	49.0	73.0
800	71.7	23.0	46.0	68.0
900	71.0	22.0	45.0	66.0
1000	69.2	21.0	23.4
1100	66.5	20.5	43.0	62.0	22.8
1200	57.7	61.3	22.4
1300	46.0	19.5	42.0	58.0	22.0
1400	33.6	57.5	21.6
1500	27.5	18.5	42.0	55.0	21.3
1600	22.4	65.0

*Static determination

Table 1.18.17—Typical Short-time Elevated-temperature
Tensile Properties of Type 318 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300
500	65.0
800
900	...	29.0	31.0	35.0
1000	36.0
1100	...	26.3
1200	54.5	...	32.0	55.0
1300	49.8	24.5	38.0
1400
1500	26.7	20.2	...	60.0
1600

Table 1.18.18 — Typical Short-time Elevated-temperature
Tensile Properties of Type 321 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	68.5	29.0	68.5	49.0	27.3	10.6	0.293
500	62.0	26.0	62.0	43.0	25.8	9.9	.300
800	57.8	21.7	57.3	37.5	23.8	9.1	.312
900	56.0	20.5	56.0	37.0	23.2	8.8	.316
1000	53.2	19.8	22.5	8.5	.320
1100	49.0	19.0	49.0	43.0	21.9	8.2	.326
1200	42.7	18.0	41.5	...	21.2	7.9	.332
1300	37.0	16.5	37.0	56.0	20.4	7.7	.338
1400	28.4	15.2	...	68.3	19.7	7.4	.343
1500	22.0	13.0	22.0	73.0	19.1	7.1	.348
1600	17.9	10.8	...	92.0

*Static determination

Table 1.18.19 — Typical Short-time Elevated-temperature
Tensile Properties of Type 321 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300
500
800
900
1000
1100
1200	51.5	23.0	17.5	20.4
1300	41.0	21.0	10.5	16.5
1400	33.0	21.0	15.0	19.5
1500	25.0	19.5	20.5	20.8
1600	18.0	...	21.0	18.5

Table 1.18.20 — Typical Short-time Elevated-temperature
Tensile Properties of Type 347 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	74.5	34.0	47.0	75.0	27.5	10.7	0.292
500	69.0	32.0	41.0	74.0	26.1	10.1	.300
800	75.5	31.8	35.0	70.5	24.1	9.2	.312
900	64.0	31.5	35.0	69.0	23.4	8.9	.316
1000	59.6	...	36.4	62.4	22.8	8.6	.320
1100	56.0	28.5	39.0	69.0	22.0	8.3	.324
1200	48.2	25.5	42.8	67.0	21.4	8.1	.328
1300	40.0	24.0	51.0	74.0	20.7	7.8	.332
1400	36.1	22.0	53.0	...	20.0	7.5	.336
1500	23.0	19.5	76.0	92.0	19.4	7.2	.340
1600	18.7	6.9	.344

*Static determination

Table 1.18.21 — Typical Short-time Elevated-temperature
Tensile Properties of Type 403 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	79.0	...	25.0	75.0	30.7	12.1	0.268
500	74.5	...	22.0	74.0	29.6	11.7	.268
800	64.5	...	22.0	71.5	27.7	10.7	.272
900	58.0	...	23.0	73.0	26.8	10.5	.276
1000	25.7	10.0	.282
1100	34.0	...	41.0	87.0	23.8	9.1	.289
1200	22.2	8.4	.300
1300	14.5	...	60.0	96.0	20.4	7.9	.316
1400
1500	9.0	...	74.0
1600

*Static determination

Table 1.18.22 — Typical Short-time Elevated-temperature
Tensile Properties of Type 405 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	62.4	38.3	35.0	70.8
500	55.2	34.4	31.5	70.9
800	46.4	32.4	26.0	69.7
900	38.4	25.6	26.0	73.3
1000	28.8	23.0	49.0	77.3
1100	21.5	21.5	41.0	73.9
1200	15.4	13.5	62.0	82.2
1300	7.7	6.9	49.0	91.0
1400	5.1	4.2	89.0	95.1
1500	3.6	2.8	105.0	97.8
1600	2.5	2.0	128.0	98.3

Table 1.18.23 — Typical Short-time Elevated-temperature
Tensile Properties of Type 410 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	79.0	...	25.0	79.0	30.7	12.1	0.268
500	74.5	...	22.0	74.5	29.6	11.7	.268
800	66.1	...	25.0	70.0	27.7	10.7	.272
900	56.3	...	26.0	73.0	26.8	10.5	.276
1000	44.8	...	26.0	78.0	25.7	10.0	.282
1100	34.7	...	43.0	87.0	23.8	9.1	.289
1200	24.6	...	50.0	93.0	22.2	8.4	.300
1300	14.8	...	58.0	95.0	20.4	7.9	.316
1400	9.2	...	68.0	98.0
1500	9.0	...	78.5	73.0
1600	8.8	...	69.0	42.0

*Static determination

**Table 1.18.24 — Typical Short-time Elevated-temperature
Tensile Properties of Type 418 Stainless Steel**

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	84.3	...	26.0	68.7
500	80.2	...	24.0	66.7
800	70.7	...	21.0	64.9
900	64.7	...	29.5	68.1
1000	52.5	...	22.5	73.6
1100	39.8	...	45.0	65.6
1200	27.1	...	26.0	90.9
1300	18.2	...	56.0	95.7
1400	11.4	...	41.0	95.2
1500	6.9	...	88.0	98.6
1600	5.7	...	145.0	94.6

**Table 1.18.25 — Typical Short-time Elevated-temperature
Tensile Properties of Type 430 Stainless Steel**

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	67.0	34.0	31.0	70.0
500	63.0	34.0	28.0	69.0
800	52.8	30.8	31.0	72.0
900	48.5	28.5	34.0	74.0
1000	35.8	...	35.5	84.0
1100	30.5	18.0	47.0	87.0
1200	18.9	...	61.5	95.0
1300	15.5	8.0	64.0	96.0
1400	7.5	...	70.0	99.0
1500	7.0	...	83.0	99.0
1600	3.5	...	188.0	98.0

Table 1.18.26 — Typical Short-time Elevated-temperature
Tensile Properties of Type 446 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity,* 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300	75.0	49.0	29.4	11.4	0.284
500	72.5	47.0	28.3	10.9	.288
800	67.8	43.8	19.0	42.0	26.0	10.0	.300
900	66.0	42.5	23.0	43.0
1000	58.0	38.3	15.0	50.0
1100	46.0	23.5	40.0	72.0
1200	20.1	13.7	57.0	86.0
1300	17.0	8.5	84.0	91.0
1400	...	5.0	87.0	98.0
1500	8.0	3.5	...	98.0
1600	4.6	3.1	127.0	98.0

*Static determination

Table 1.18.27 — Typical Short-time Elevated-temperature
Tensile Properties of Type 501 Stainless Steel

Temperature, °F	Tensile strength, 10 ³ lb/sq in.	Yield strength (0.2% offset), 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
300
500	64.6	...	28.5	78.0
800	62.0	...	26.0	76.0
900
1000	51.1	...	22.0	73.0
1100
1200	32.5	...	26.0	86.0
1300
1400
1500
1600

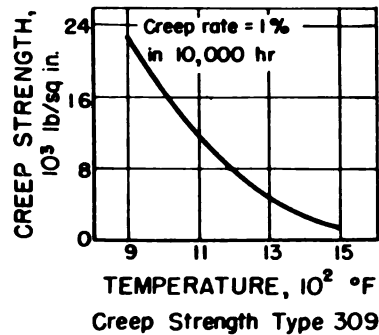
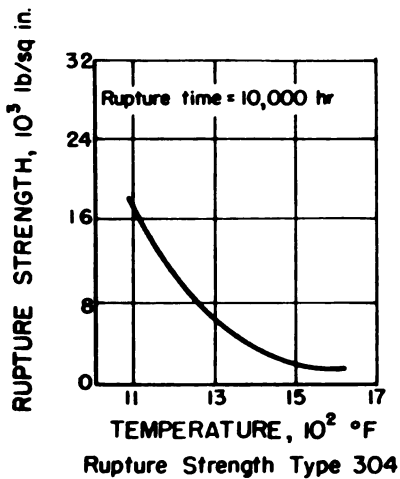
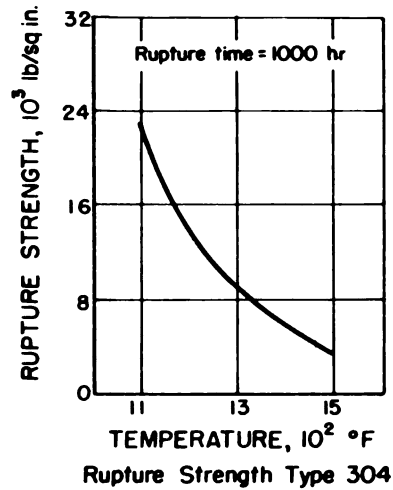
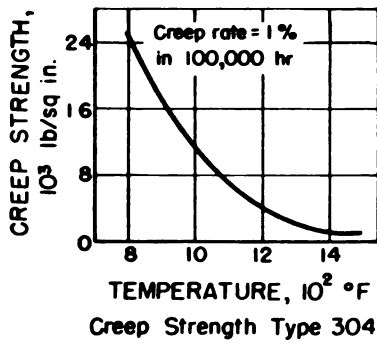
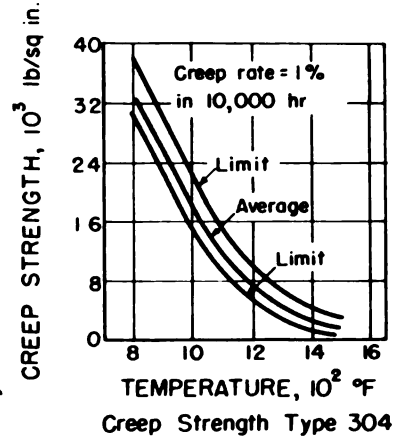
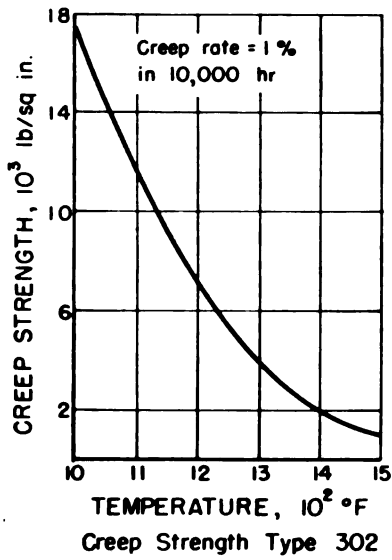


Fig. 1.18.1—Data on Creep and Rupture Strength of Various Stainless Steels.
Prepared from data of ASTM Publication No. 100.

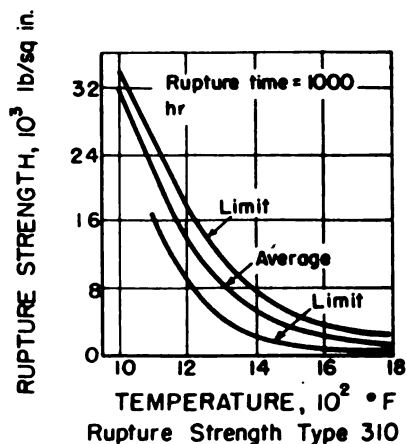
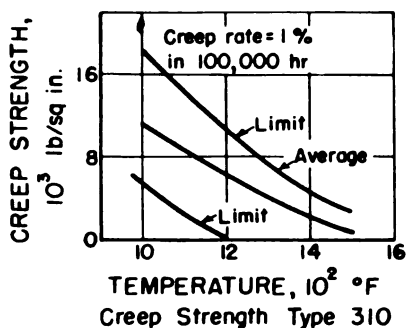
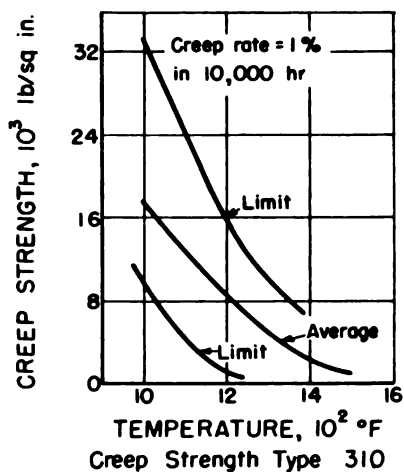
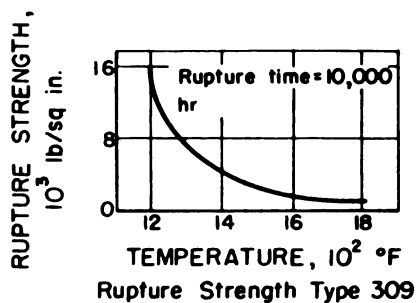
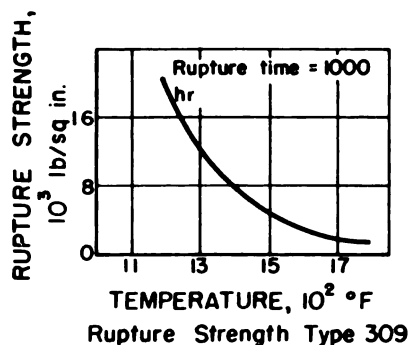
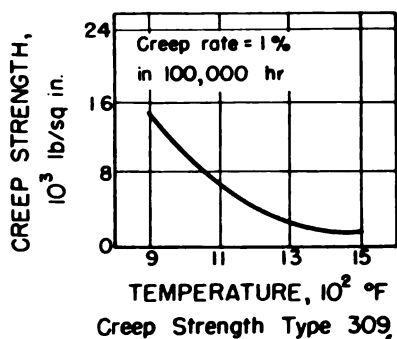


Fig. 1.18.2 — Data on Creep and Rupture Strength of Various Stainless Steels. Prepared from data of ASTM Publication No. 100.

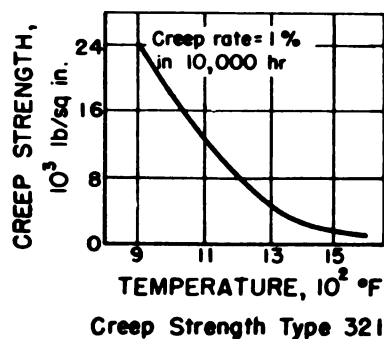
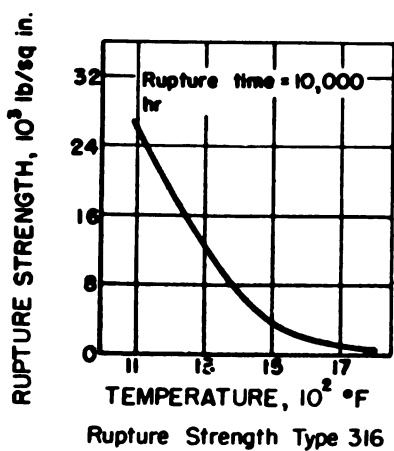
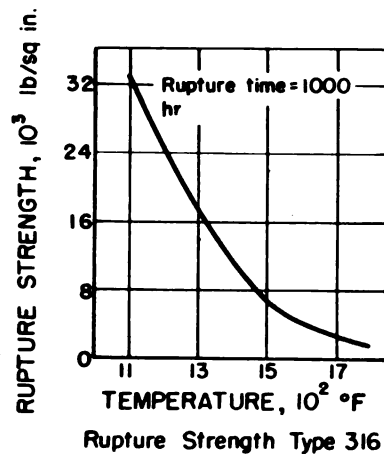
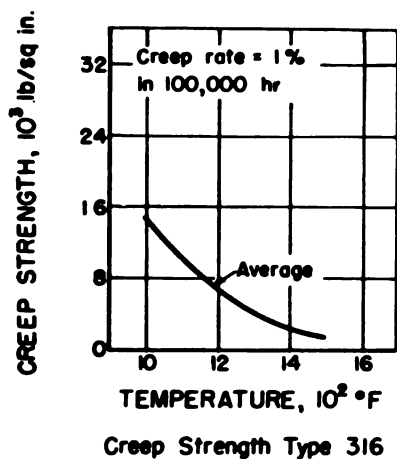
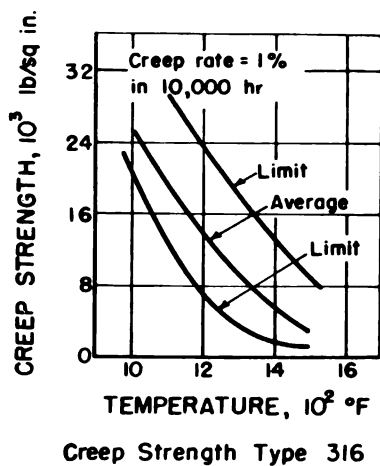
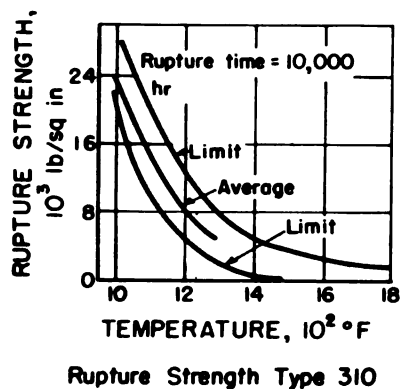


Fig. 1.18.3—Data on Creep and Rupture Strength of Various Stainless Steels.
Prepared from data of ASTM Publication No. 100.

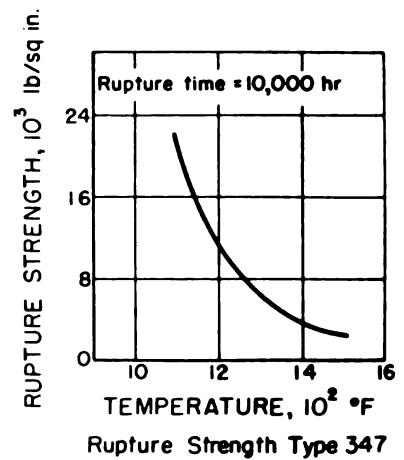
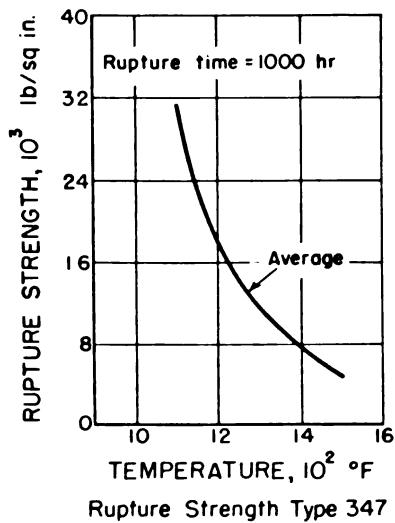
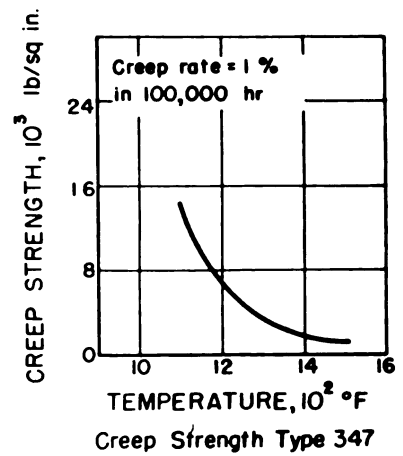
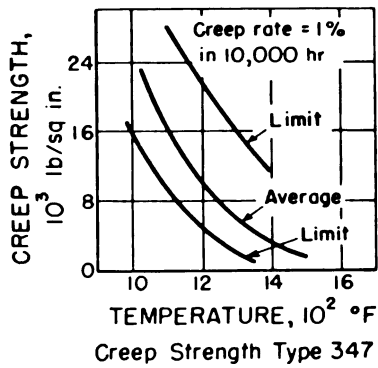
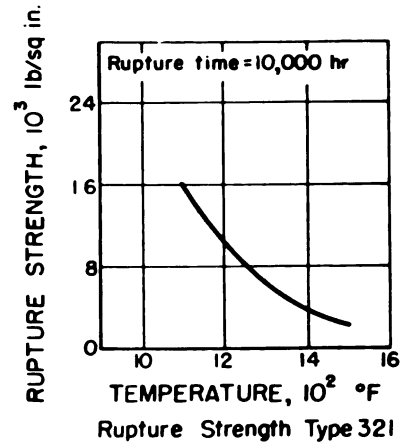
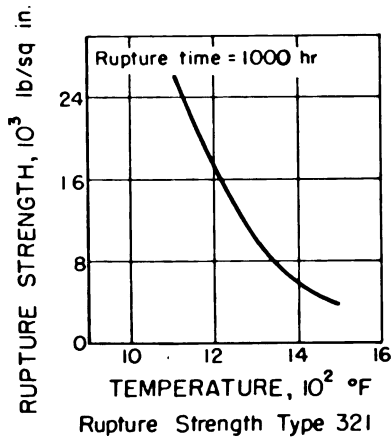


Fig. 1.18.4 — Data on Creep and Rupture Strength of Various Stainless Steels. Prepared from data of ASTM Publication No. 100.

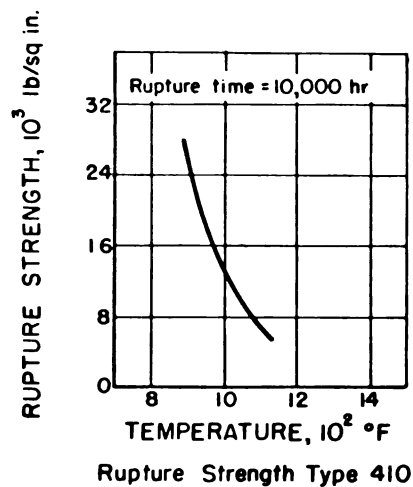
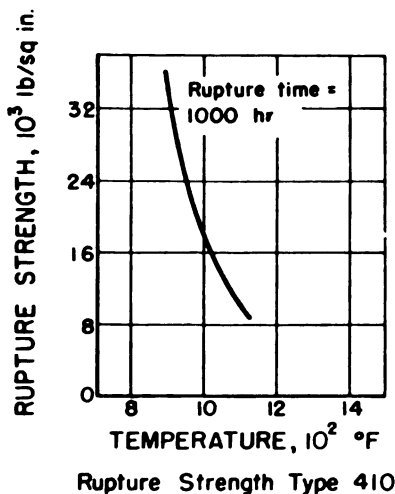
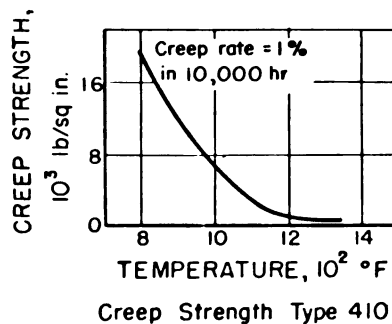
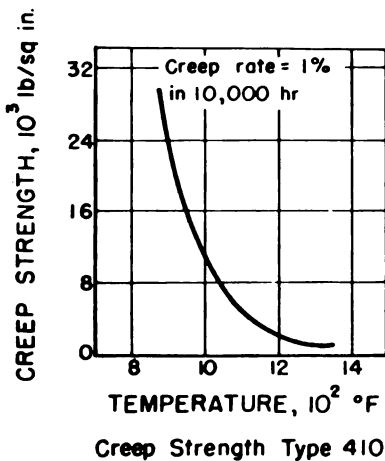
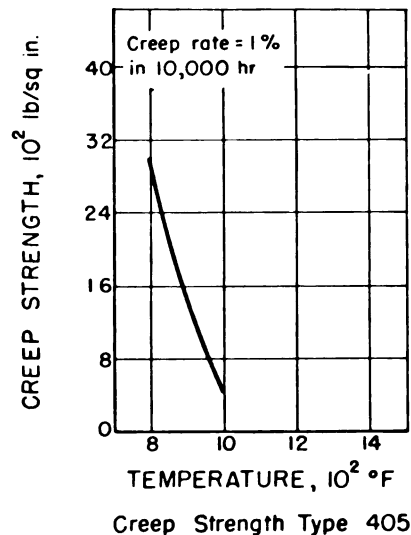
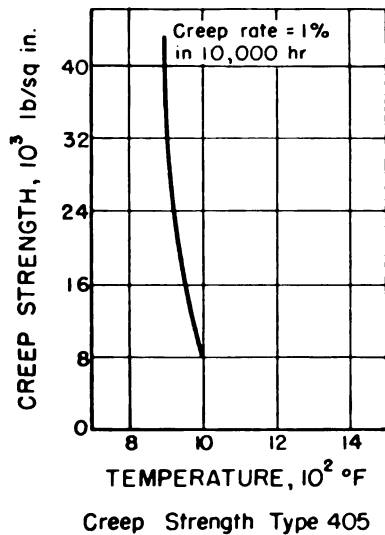


Fig. 1.18.5 — Data on Creep and Rupture Strength of Various Stainless Steels.
Prepared from data of ASTM Publication No. 100.

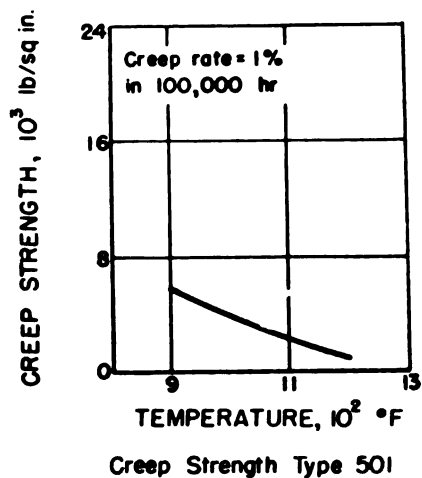
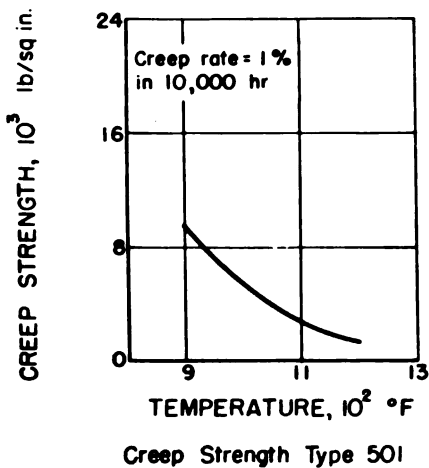
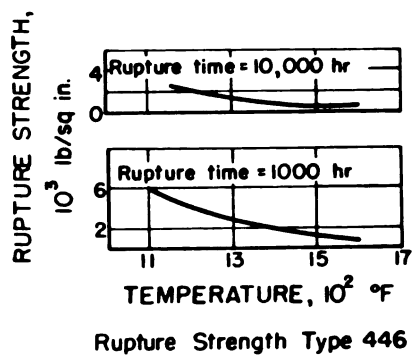
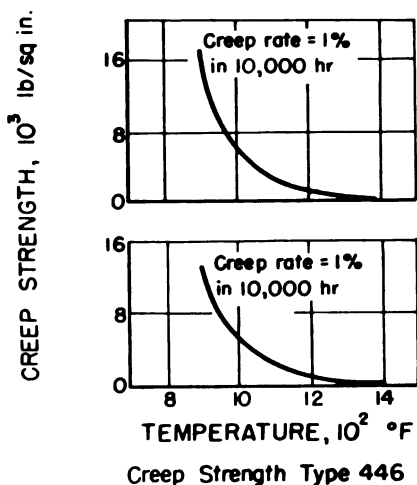
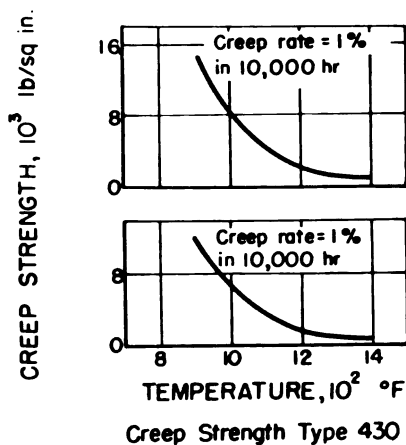
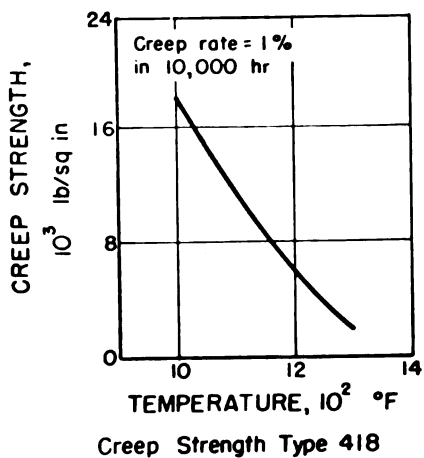


Fig. 1.18.6—Data on Creep and Rupture Strength of Various Stainless Steels. Prepared from data of ASTM Publication No. 100.

MELTING AND CASTING

Special techniques are necessary to melt stainless steels because of their high chromium contents. Chromium at steel-making temperatures has a great affinity for both oxygen and carbon, and under some melting conditions, chromium may also absorb nitrogen from the air. In fact, its affinity for oxygen is so great that chromium will be oxidized from a melt in preference to carbon* or iron. Therefore, if normal decarburizing procedures employing oxygen were used, chromium would be removed instead of carbon. In many stainless steels, a low-carbon content is desired because a small quantity of carbon will tie up a relatively large amount of chromium and render it ineffective for imparting corrosion resistance. Also, the presence of carbon results in the formation of carbides which embrittle the steels and reduce the corrosion resistance by virtue of the difference in electrical potential between the carbide and the base material.

Most stainless steel is made by the basic electric-arc process, although some alloys are made by the acid electric-arc process. When an alloy is made by either electric-arc process, a furnace of the Héroult type is usually used. The initial charge consists of low-phosphorus steel scrap. If an austenitic alloy is being melted, nickel is included in the initial charge because it is unaffected by oxygen and carbon. Iron ore or mill scale is then added to reduce the carbon content through the formation of CO. An oxidizing slag is used. When the carbon content is reduced to the desired level, the oxidizing slag is removed, and a finishing slag is placed on the melt. The steel is then deoxidized with ferrosilicon. Low-carbon ferrochromium is added to the melt at this time, making sure that not enough is added at one time to cause the melt to "freeze." When all the ferrochrome is melted, various other alloying additions are made to achieve the desired alloy composition. The steel is then further deoxidized prior to pouring. Certain additions, such as titanium, generally are made in the ladle.

The induction furnace usually is used in the remelting of low-carbon stainless-steel scrap. This type of furnace is used because: (1) No carbon electrodes are needed, eliminating any carbon pickup from this source, and (2) the melt, if necessary, can be covered by a reducing or inert atmosphere, minimizing the loss of chromium by oxidation.

Stainless steels to be fabricated into wrought material are usually poured into permanent ingot molds. The steel is poured at about 2900°F, and when pouring is complete, an exothermic mixture is placed on top of the riser to keep the metal molten in the hot top, thereby feeding the solidifying ingot. Titanium-bearing alloys are generally poured at a higher temperature because of the formation of an oxide film which decreases their fluidity. Also, periodic titanium additions are needed to maintain the required titanium level. Some difficulty has been encountered with stringers of inclusions in thin sections of the titanium-bearing alloys.

Intricate castings used in the as-cast condition are usually poured in sand molds. The pouring procedure and the use of exothermic mixtures or risers are very similar to those used for casting in permanent molds.

FORMING AND FABRICATION

FORGING

The forging characteristics of stainless steels depend upon their composition. Generally, all well-known grades of stainless steels can be forged, though special care is needed during the forging operation. Because of the low heat conductivity of these alloys, the ingot

*This is true at normal steelmaking temperature. When a large degree of superheat is used in melting, the opposite has been found to be true. This is the basis for the so-called "rustless process" of melting stainless steels.

soaking period must be long enough to ensure a uniform temperature throughout the ingot. This means that longer soaking periods are necessary than those used for plain carbon and low-alloy steels. Also, since stainless steels have higher strength and hardness at elevated temperatures than mild steel, more and heavier blows are necessary to form stainless steels into a given shape.

When forging a martensitic-type stainless-steel alloy, the alloy must be cooled slowly through the transformation range after forging to prevent cracking caused by the differential expansion which occurs in the alloy during the transformation of austenite to pearlite or martensite.

Ferritic stainless steels must be forged at a finishing temperature low enough to prevent excessive grain growth. The cooling rate after forging this type alloy is unimportant from the standpoint of cracking because no phase changes take place. However, if these alloys are not heat treated after forging, carbide precipitation, which will lead to embrittlement or intergranular corrosion in the presence of certain corrosive media, must be prevented or at least minimized.

Recommended forging temperatures range from 2000° to 2250°F for initial forging to 1300° to 1800°F for finishing.

EXTRUSION

The extrusion of stainless steels is a recent innovation based on a French process using molten glass as a lubricant. As yet, there are no data available on the extrusion conditions.

DRAWING

AUSTENITIC ALLOYS

Austenitic grades of stainless steels lend themselves to forming and deep-drawing operations. These alloys possess high tensile strength and good ductility. They are also stiffer plastically than ordinary steels and work harden much more rapidly. Because of these inherent characteristics, more power is required to draw austenitic alloys than ordinary steels (approximately $1\frac{1}{2}$ times that needed for mild steel). Dies used in drawing stainless steels are of the high-carbon chromium type. For wire drawing, alloy-steel dies with carbide inserts are also used. Many different types of lubricants are used for this work, some of the more common being lard oil and sulfur, lithopone and talc, mutton tallow, castor oil, soft soap, varnish, and shellac.

Deep Drawing

Draws of 40 to 45 percent are common for austenitic alloys, and draws as high as 50 percent are obtained very often. The controlling factors during drawing are the tensile and yield strengths of the alloy, elongation as retained during cold working, and factors common to die forming such as tools and lubricants.

The rate of work hardening during drawing is a particularly important factor. The martensite and ferritic stainless steels behave comparably to deep drawing carbon steels. These stainless steels are inherently harder than carbon steels and require more power and heavier lubricants. The austenitic stainless steels work harden much more rapidly and consequently require more power and frequent anneals.

Wire Drawing

Because of the rapid work hardening of the chromium-nickel austenitic stainless alloy, wire must be annealed after a 50- to 65-percent reduction, although in fine wires, up to 80-percent reduction before annealing may be permitted. Annealing is done by subjecting the wire to a heat treatment of from 1725° to 1750°F. The actual drawing schedule of the wire depends on the size of the finished wire and the required strength.

CHROMIUM ALLOYS

Forming of straight chromium-type alloy usually is limited to Types 403, 405, 410, and 430. Except for the higher power requirements, performance in general is similar to that of plain carbon steels. Other grades of these chromium alloys exhibit physical characteristics which are not conducive to good formability.

ROLLING

HOT ROLLING

The principal differences in hot-rolling stainless steels compared with hot rolling plain carbon and low-alloy steels are the slower rolling speeds and greater roll power required and the smaller reductions per pass. These differences are a result of the high strength of hot stainless steels compared with that of ordinary steels. Using the conventional practices for hot-rolling ordinary steels modified by the factors just outlined as well as the temperature restrictions mentioned in the discussion of forging, stainless steels can be processed into blooms, billets, slabs, and sheet-bar. Hot-rolling temperatures for stainless steels are generally about 50°F lower than the forging temperatures.

COLD ROLLING

Stainless-steel sheet and strip are cold-rolled to produce a better surface finish; this operation also increases the strength and hardness. Rolling is often done in a four-high mill, and the tension between rolls must be adjusted carefully to avoid slippage between the work and the rolls as this would be harmful to the surface. Because of rapid work hardening of the austenitic-type alloy, it is often necessary to give the rolled material one or more intermediate anneals during processing.

POWDER METALLURGY

Stainless-steel parts can be fabricated by two powder-metallurgy methods. In the first, carbonyl iron and nickel and electrolytic chromium powders are mixed in proper proportions to give the desired alloy composition. The mixture of powders is then compacted at high pressure and sintered in a reducing atmosphere at high temperature for a relatively long time to allow the alloying elements to diffuse throughout the iron. Typical conditions are: compression of the powder mixture at 140,000 lb/sq in. and sintering of the compact at 2400°F for 44 hr in an atmosphere of highly purified hydrogen. Material fabricated in this manner has a slightly inferior resistance to corrosion because of its inherent porosity; however, manganese and other high-cross-section elements can be eliminated from the alloy. The mechanical properties of powder-metallurgy material are lower than those of cast stainless steel which has received the same treatment, as is shown in Table 1.18.28.

The second method of fabrication is to compress prealloyed powders. These powders can be made by "shotting" an alloy of the desired composition or by sensitizing certain alloys and then subjecting them to intergranular corrosion by a copper sulfate-sulfuric acid solution. Metal loss in powders prepared by the latter method can be kept to 5 percent. The advantage of using prealloyed powders is that the sintering time and temperature can be reduced sharply because the amount of diffusion necessary is decreased.

Powder metallurgy offers a convenient method of fabricating small, complicated parts to close tolerances without a large amount of machining.

Table 1.18.28 — Comparative Physical Properties of Powder-metallurgy and Cast 18-8 Stainless Steel

(Research Report 99, Hardy Metallurgical Company)

Test specimen	Yield strength, 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Hardness, Brinell number	Izod impact strength, ft-lb
Powder compact	29 - 33	63 - 66	30 - 40	40 - 50	123 - 133	55 - 69
Cast	35 - 45	80 - 90	55 - 60	55 - 65	135 - 185	70 - 110
Hard-drawn wire (from cast)		300(min)				
Hard-drawn wire (from powder)		303				
Soft-annealed wire (from powder)		107 - 109	33 - 44*			
Soft-annealed wire (from cast)		100 - 130	38 - 58*			

*In 10 in.

JOINING

Stainless steel can be joined by soldering, brazing, copper-brazing, and welding.

SOLDERING

Soldering (more often called "soft-soldering") is the lowest-temperature method of joining stainless steel. The use of stainless steel joined by soldering is limited, however, by the melting point and strength of the solder. Lap, sleeve, and lock joints are usually used for soldering to increase the shear strength of the joint. Very often soldering is used in conjunction with spot welding, tack welding, and riveting to ensure tightness of joints to hold liquids and gases. Mixtures of tin and lead, 50-50, 60-40, and 80-20 are used for soldering stainless steels. All grades of stainless steel can be soldered.

Surface preparation is very important in soldering. The surface should be cleaned of all loose oxide and grease, and a strong acid flux, such as HCl or ZnCl₂ and NH₄Cl, should be used. In many cases it is very helpful to first tin the pieces to be soldered. A large soldering iron or torch should be used to heat the area being soldered because of the low heat conductivity of stainless steel. After soldering, it is very important that any remaining flux be removed because chloride ions attack stainless steels quite readily. This can be done by washing the joint with a dilute solution of ammonia followed by plain water.

In most corrosive media, there is apt to be a large difference in potential between the solder and the stainless steel. This would lead to rapid corrosion of the solder. Therefore, care must be exercised when soldered stainless-steel joints are specified for exposure to corrosive media.

BRAZING

SILVER-BRAZING

Silver-brazing (silver-soldering) can be performed on all types of stainless steel. Joints made by this process are stronger than soldered joints. The melting points of the commercially available brazing alloys depend on their composition, but practically all of them melt in the range 1000° to 1500°F.

Because of the relatively high temperatures required, the effect of brazing temperature on the various types of stainless steels must be considered. When the austenitic type of alloy is silver-brazed, the joint is heated into the carbide-precipitation temperature range (800° to 1500°F). Therefore, when this type of alloy is to be silver-soldered, it is good practice to braze as quickly as possible so that the alloy is held within the carbide-precipitation range for as short a time as possible to minimize the effect of carbide precipitation. The use of stabilized austenitic steels (Types 321 or 347) when brazing is to be done, will eliminate this difficulty. However, if stresses occur during brazing, molten silver-solders and copper tend to penetrate Type 347 stainless steel in an intergranular manner. Consequently, care should be taken in silver-soldering or brazing stressed sections of Type 347 stainless.

When silver-soldering a martensitic type of alloy which will air-harden upon cooling, it is desirable to employ a brazing alloy which melts below the transformation temperature of the stainless-steel alloy. A ferritic-type alloy should be brazed at as low a temperature and in as short a time as possible to prevent excessive grain growth.

When two pieces of stainless steel are to be silver-brazed, the joint surface should be first cleaned and degreased, then a brazing flux should be applied. Many brazing fluxes, usually consisting of a mixture of fluorides and borates, are commercially available. In many cases, it is advisable to use fixtures to align the pieces to be brazed because of the high temperatures involved. The joint is then heated (an acetylene torch can be used), and the brazing alloy is applied. When the joint cools, it should be cleaned of any residues of flux and oxide.

COPPER-BRAZING

In copper-brazing, pure copper is usually used as the brazing material, and therefore, temperatures of 2050° to 2100°F are needed to melt and flow the copper by wetting and capillary action. Because of the high temperatures involved, special consideration must be given to the cooling cycle of austenitic and martensitic stainless steels as discussed previously. Ferritic steels are usually not copper-brazed because of the possibility of grain growth.

The procedure for copper-brazing is very similar to that used for silver-brazing, the major differences being that: (1) Generally, no flux is used in copper-brazing and (2) copper-brazing is done in a dry hydrogen atmosphere to avoid oxidation of the steel at the joint.

WELDING

Welding is by far the most important means of joining stainless steels. Both fusion-welding methods and resistance methods can be used. Table 1.18.29 lists welding processes which are applicable to stainless steels and the form of material to which they can be applied.

NICKEL-CHROMIUM ALLOYS

All types of austenitic alloys can be welded with relative ease with the exception of the free-machining grades (Type 303). This alloy is subject to porosity in weldments because of the additions made to improve the free-cutting properties.

Because portions of the welded structure are heated and cooled through the carbide precipitation zone (800° to 1600°F), special techniques must be used in welding this type of alloy if corrosion resistance is important. This problem can be handled in two ways. The first is a post-weld heat treatment at about 2050°F for about 2 hr to put the carbides into solution; if the alloy is then quenched, most of the carbides will be retained in solution. The second method is to use a stabilized stainless steel (Type 321 or 347). The latter method is preferable because it eliminates the carbide-precipitation problem entirely if stabilization is complete. However, just the use of a stabilizing addition such as niobium

Table 1.18.29 — Welding Processes* Applicable to the Various Forms of Stainless Steel
(Stainless Steel Handbook, Allegheny-Ludlum Steel Corporation)

Welding methods	Plate	Sheet	Strip	Bar	Tubing	Wire	Forgings	Castings
Metallic arc	U	U	U	U	U		U	U
Inert arc	P	U	U	P	U	P	P	
Atomic hydrogen	P	U	U	P	U			
Oxygen acetylene	P	U	U		P	P		
Resistance methods								
Spot and projection	P	U	U					
Line seam		U	U					
Flash and upset butt	P	U	U	U	U	U		

*U represents most usual application; P represents possible, but less usual, application

or titanium is not the safest practice. Stabilization heat treatment at 1700°F for about 4 hr is often practiced although some investigators discourage this procedure because of the possible formation of the sigma phase. If the material has been held at temperatures of the order of 1000° to 1500°F, a homogenization treatment at 2050°F should precede the stabilization treatment at 1700°F.

It is beyond the scope of this chapter to discuss procedures for all possible welding methods. In general, welding procedures are the same as those used for plain carbon and low-alloy steels. For detailed information of a specific welding process, the *Welding Handbook*¹ should be consulted.

STRAIGHT CHROMIUM ALLOYS

Generally, the following martensitic- and ferritic-type alloys are considered weldable: Types 403, 405, 410, 418, 430, 431, and 446. (Types 405, 430, and 446 are ferritic-type alloys, while the others are martensitic-type alloys.)

The straight chromium alloys require preheating before welding to prevent weld cracking. However, prolonged heating over 1600°F is conducive to grain growth and should be avoided if possible when welding the ferritic type of alloy. The grain size of the ferritic-type alloy can be refined only by cold work. Usually, this is not feasible for a welded structure.

The straight chromium grades of stainless steel are subject to embrittlement under welding heat. To restore ductility, it is necessary to anneal these alloys after welding, (see discussion of "Heat Treatment").

MACHINING

Stainless steels, in general, are much more difficult to machine than ordinary steels because they are stronger and usually tougher than mild steels. The austenitic grades work-harden more rapidly than the carbon steels. Accordingly, the power requirements of the machine are higher, cutting speeds are lower, and cutting feeds are usually higher. Higher cutting feeds are especially recommended when machining austenitic-type alloys because of the rapid work-hardening which takes place.

Of the three general types of stainless steels, the ferritic type has the best machinability. Tool life with both carbide and high-speed steel tools is excellent. The martensitic-type alloy has the next best machinability. Tool life with a high-speed steel tool is excellent but with a carbide tool is very poor.

¹Reference appears at end of chapter.

The poorest machinability is exhibited by the austenitic-type alloys. Tool life using either type tool is very poor. Table 1.18.30 compares the machinability of various types of stainless steel with that of mild steel.

Table 1.18.30 — A Comparison of the Machinability of Various Stainless Steels With Mild Steel

Type of alloy	Machinability, * %
Free-machining ferritic alloys	90
Free-machining martensitic alloys	85
Free-machining austenitic alloys	75
Ferritic alloys	55
Martensitic alloys	50
Austenitic alloys	40

*Mild steel is rated as 100%

Although the stainless steels in general and the austenitic grades in particular are more difficult to machine than ordinary steels, industry has adequately solved the problems, and with proper precautions a very satisfactory job can be done. Free-machining grades of certain austenitic, ferritic, and martensitic type of alloys are available. These alloys usually contain high selenium and phosphor or high sulfur to improve the machining characteristics. However, machinability is improved at the expense of corrosion resistance, and therefore, these alloys cannot be used in the presence of strong corrosive media.

Another criterion of machinability is often the quality of surface finish. With high-speed steel tools, surface finish is likely to be poor despite good tool life. On the other hand, using carbide tools is likely to result in a satisfactory surface finish.

HEAT TREATMENT

Table 1.18.31 gives the annealing conditions for various types of stainless steels, while Table 1.18.32 gives the hardening conditions for the martensitic-type alloy. The austenitic and ferritic types of alloy can only be hardened by cold work. Water-quenching is preferred for austenitic grades in order to retain the carbon in solution.

Within recent years, age-hardenable stainless steels have been developed. They are of special analyses and as yet not used extensively.

CORROSION BEHAVIOR

The alloys of iron, chromium, and nickel are the most versatile nonprecious corrosion-resistant alloys. It is believed by most investigators that the corrosion resistance of these alloys results from the presence of a thin oxide or hydrate film on the surface of the alloy which is stabilized by chromium. It is agreed generally that passivation is not a continuous state and that it exists only in certain environments or under certain conditions. Under many conditions, the range of passivity is broad, while in others the range is relatively narrow and may be destroyed by slight environmental changes.

The straight chromium irons derive their resistance to rusting in the atmosphere and to oxidation at high temperatures from the presence of chromium. They possess fairly good resistance to rusting if their chromium content is above 12 percent. With higher chromium contents (more than 18 percent), they become passive in the atmosphere without

Table 1.18.31 — Annealing Conditions for Various Stainless Steels

AISI type no.	Annealing range, °F	Cooling rate*
301	1950–2050	WQ†
302	1850–2050	WQ†
302B	1850–2050	WQ
303	1800–2000	WQ
304	1850–1950	WQ†
305	1800–1950	WQ†
308	1800–2050	WQ†
309	2000–2100	WQ†
310	2050–2150	WQ†
316	1950–2150	WQ†
317	1950–2150	WQ†
318	1975–2150	WQ
321	1800–2000	WQ†
347	1800–2000	WQ†
403	1500–1600	SFC
405	1300–1500	AC
410	1500–1600	SFC
414	1200–1300	FC
416	1500–1650	FC
418	1500–1600	FC
420	1550–1650	SFC
420F	1550–1650	SFC
430	1400–1550	FC
430F	1250–1400	FC
431	1150–1250	FC
440A	1550–1650	FC
440C	1550–1650	FC
440F	1550–1650	FC
442	1300	WQ or AC
446	1450–1600	WQ

*WQ = water quench; AC = air cool; FC = furnace cool; SFC = slow furnace cool

†Thin sections may be air cooled

Table 1.18.32 — Hardening Heat Treatment for Martensitic Stainless Steels*

AISI type no.	Hardening range, °F	Cooling rate†
403	1700–1850	O or A
410	1700–1850	O or A
414	1800–1900	O or A
416	1700–1800	O or A
418	1800	O or A
420	1850–1900	O or A
420F	1850–1900	O or A
431	1750–1850	O or A
440A	1850–1900	O or A
440C	1850–1900	O or A
440F	1850–1900	O or A

*Tempering for intermediate hardness is done at from 1000° to 1400°F, depending on the required hardness; for stress relief, draw below 700°F

†A = air cool, to be used for thin sections; O = oil quench

developing even a thin film of rust. Additions of silicon and aluminum improve the resistance of the chromium irons to oxidation at elevated temperatures.

Nickel is added to render the alloys austenitic because of useful mechanical properties and to expand the passivity limits of the chromium irons. Better resistance to nonoxidizing media and to many neutral salt solutions is possessed by alloys having high nickel contents.

Additions of molybdenum to chromium irons and to the austenitic chromium-nickel alloys tend to strengthen the passive film under conditions where it is likely to fail. Molybdenum also improves the resistance of these alloys to pitting. However, additions of molybdenum tend to decrease the corrosion resistance of these alloys in strongly oxidizing environments.

Niobium, titanium, and vanadium are added to stainless alloys to combine with carbon, thus stabilizing the alloys against intergranular-type corrosion. Additions of these elements, however, frequently reduce the general corrosion resistance of the alloys.

In addition to the alloy compositions, changes in microstructure brought about by different heat treatments have considerable effect on their corrosion resistance. These alloys exhibit greater resistance when the carbon is completely in solution producing a homogeneous single-phase structure. The martensitic compositions normally show maximum resistance in the fully hardened condition, while the austenitic compositions exhibit a wide range of passivity when cooled rapidly from temperatures within the range 1850° to 2000°F. Rapid cooling from the heat-treating temperature is essential to prevent carbide precipitation from the austenitic solid solution.

WATER

Stainless steels are normally passive in natural fresh water, mine waters, boiler condensate, and steam at elevated temperatures. Under the usual conditions of exposure, these alloys remain substantially free of rust and pits. However, improper heat treatment or strong cell concentrations may bring about superficial rusting or incipient pitting.

An important use of stainless steels in reactor engineering is that of a container for high-purity water containing various amounts of dissolved oxygen from room temperature to 600°F or higher. In static tests, the austenitic alloys possess excellent resistance at room temperature and 200°F, while the martensitic and ferritic chromium irons exhibit various degrees of rusting. As the temperature is increased to 500° and 600°F, the stainless steels acquire a dark tarnish film which sometimes develops into a loose powdery red rust coating upon extended exposures. This is particularly true when the water contains a considerable amount of dissolved oxygen. In most cases, there is little or no difference in weight change between those samples exhibiting a tarnish film and those possessing a powdery coating of red rust. This, together with the fact that numerous autoclaves constructed of stainless steels have been in operation for several years without serious attack, indicates that the corrosion of stainless steels is not of sufficient magnitude to cause any serious loss in mechanical properties. However, under reactor operating conditions, the presence of even a small amount of corrosion product (loose red rust) might result in film build up which would seriously affect flow and heat-transfer characteristics.

In order to increase wear resistance of structural materials, considerable attention has been given to the possible use of nitrided stainless steels for service in high-temperature water. The problems connected with corrosion of nitrided stainless steels (either uncoupled or coupled with other materials) are far from a satisfactory solution. The nitrided materials exhibited severe rusting, especially when exposed to low-temperature water (room temperature and 200°F), with the higher oxygen concentrations being somewhat more corrosive. At 500°F, indications are that high-temperature oxygenated water may passivate the nitrided surface and thus increase resistance to corrosion. To date, the reported data indicate rather strongly that the behavior of nitrided stainless steels in water

is highly erratic. Detailed results on the corrosion of nitrided materials can be found in report BMI-742.

Preliminary static tests and dynamic-loop tests indicate that the corrosion rate of austenitic stainless steels is markedly reduced in the presence of 100 to 500 cm³ dissolved hydrogen/liter at temperatures of 500° to 600°F.

STEAM

Steam temperatures influence the corrosion rate of stainless steels. Pressure changes ranging from 100 to 1200 lb/sq in. have no influence on the type or rate of corrosion on stainless steels. The temperature at which excessive corrosion begins increases with the chromium content of the stainless steels. The 18-8 type alloys exhibit the same rapid corrosion above their limiting temperature of 1670°F as do the lower chromium steels at lower temperatures. Corrosion tests conducted in steam reveal that 25 chromium-20 nickel alloys with and without 2 parts of tungsten exhibit practically no corrosion after 500 hr at 1750°F. Additional exposures (up to 1300 hr) indicate that these alloys are extremely resistant to steam corrosion. In other tests in steam at 1800°F, the 25 chromium-20 nickel alloy lost only 0.11 percent of its original weight in 1300 hr.

ATMOSPHERE

Chromium-iron and austenitic cobalt-nickel alloys retain a large portion of their luster when exposed to average urban or rural atmospheres. They become moderately stained in low-sulfur industrial atmospheres. As the sulfur content of the atmosphere increases, they become more heavily discolored. Marine atmospheres also discolor stainless steels. The most resistant are the austenitic chromium-nickel alloys and the high-chromium (18- to 30-percent) irons. The addition of molybdenum to the 18-8 alloys is beneficial in marine atmospheres and industrial atmospheres high in sulfur.

The effect of surface conditions and heat treatment is often mentioned in connection with the corrosion behavior of the stainless sheets in air. Studies have revealed that 18-8 type alloys behave much the same whether quench annealed or sensitized, while the chromium-irons are somewhat better when hardened than when annealed. In high-sulfur atmospheres, ground surfaces are somewhat less satisfactory than pickled or buffed surfaces.

OXIDATION RESISTANCE

The resistance to scaling and oxidization offered by stainless steels to oxidizing gas atmospheres (sulfur free) at high temperatures is a function of their chromium content. Other elements, such as silicon and aluminum, are often added to increase the oxidation resistance of the stainless steels. A general indication of the influence of chromium on the oxidization resistance of stainless steels may be obtained from an examination of Fig. 1.18.7. When 25 to 30 percent of chromium is present, the alloys resist scaling at temperatures as high as 2012°F. The stainless steels most frequently used for high-temperature service are Types 309, 310, 330, and 446, since these steels exhibit superior resistance to oxidization. Corresponding heat-resisting alloy castings used in this type of service include Types HE, HH, HI, HK, HT, HV, HW, and HX. Lower-chromium alloys are also used at high temperature; however, their useful temperature range is 1500°F or below. Approximate temperatures at which stainless steels are considered resistant to scaling under most conditions are listed in Table 1.18.33.

The presence of sulfur in high-temperature oxidizing gases is not serious as long as the chromium content of the alloy is high. With nickel present in the alloy, the chromium content should be at least 25 percent. Corrosion by sulfur is more severe under reducing conditions than under oxidizing conditions, since sulfide-corrosion products are less protective than oxides. Reported data indicate that the higher the chromium content, the more severe are the sulfur conditions that can be resisted successfully.

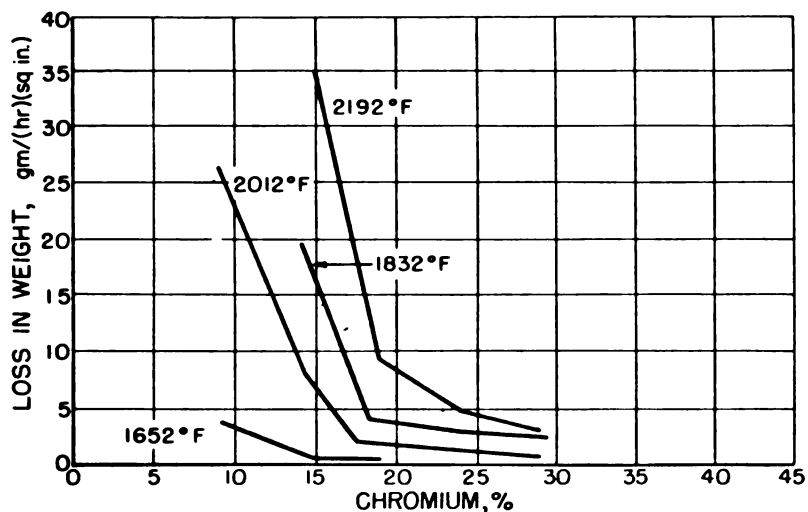


Fig. 1.18.7—Influence of Chromium on the Scaling Resistance of Steels. Reprinted from Stainless Steel Handbook, Allegheny-Ludlum Steel Corporation.

Table 1.18.33 —Oxidation Resistance of Stainless Steels

AISI and ASTM designation	Maximum temperature for continuous operation with good resistance to scaling and oxidation, °F
301	1650
302	1650
303	1650
304	1650
305	1650
308	1700
309	2000
310	2100
316	1700
317	1700
318	1700
321	1700
347	1700
403	1250
405	1300
410	1200
414	1250
416	1250
418	1300
420	1200
420F	1200
430	1500
430F	1550
431	1600
440A	1400
440C	1400
440F	1400
442	1800
446	2050

In addition to the stainless steels, super heat-resisting alloys are becoming increasingly important where high strength and good oxidation resistance are necessary. In addition to 12 to 20 percent chromium, many of these alloys contain large amounts of cobalt and nickel with smaller additions of molybdenum, tungsten, niobium, titanium, aluminum, and silicon. The superior creep resistance of these alloys makes these alloys advantageous for service at high temperature.

LIQUID METALS

In general, the chromium-iron and austenitic chromium-nickel alloys are not useful in handling molten metals, such as zinc, tin, solder, babbitt, copper, brasses, aluminum, bismuth, lithium, bismuth-lead, bismuth-indium, and lead. Possible exceptions are molten sodium and molten lead under certain conditions. The corrosive attack on the stainless steels by liquid metals is believed by many investigators to be due primarily to intergranular attack which causes brittleness. However, in many cases, a uniform alloy layer is also observed on the surface of the alloys after exposure to molten metals.

Stainless steels in general exhibit acceptable resistance to liquid sodium (and sodium-potassium melts) at elevated temperatures, provided the oxygen content of the liquid sodium is below 0.02 percent. When this oxygen content is exceeded, measurable corrosion will occur. Of course, these higher oxygen contents can be gettered by additions of calcium. In addition to static tests, thermal loops have been operated successfully with liquid sodium in contact with stainless steels. The carbon content, in addition to the oxygen content, of the liquid sodium should be kept to a minimum. Liquid sodium containing carbon will carbonize the surface of stainless steel.

On the basis of static weight changes, Types 304, 310, 316, 321, and 347 appear to resist molten potassium satisfactorily at elevated temperatures (1400° to 1600°F).

Molten lithium appears to be more corrosive than molten sodium. Data indicate that the chromium-irons are more resistant than the austenitic chromium-nickel alloys; however, none are entirely satisfactory for service at 1830°F.

In addition to liquid lithium, molten bismuth, lead, and mixtures of bismuth and lead and bismuth-iridium and lead are very corrosive to stainless steels at elevated temperatures. Other investigations have reported attack of stainless steels by molten bismuth, molten lead, and mixtures of lead and bismuth at temperatures as low as 1000°F. Here, as in the case of lithium, more attack is noted on the alloys containing nickel than on the straight chromium alloys. Thus, the Type 446 chromium-iron alloy is more resistant than the austenitic grade.

MOLTEN CAUSTIC

In general, stainless steels and super heat-resisting alloys are attacked severely by molten caustics. In addition to heavy scale formation, the alloys are subject to the phenomenon of mass transfer. The mechanism by which this occurs is still not understood thoroughly.

For the most part, work on moderator coolants has been confined to corrosion studies involving alkali and alkaline-earth hydroxides in contact with several types of stainless steels. Corrosion studies have indicated that sodium hydroxide is about the most corrosive of the hydroxides examined. Corrosion data obtained at 1470°, 1500°, and 1830°F indicate that when in contact with sodium hydroxide, stainless steels show a surface penetration of 7 to 16 mil in 100 hr. Potassium and lithium hydroxides are somewhat less corrosive (6 to 7 mils penetration). The attack by barium and strontium hydroxides is of the same order of severity as that obtained for potassium hydroxide (5 to 7 mils).

To date, most of the corrosion data have been obtained using commercial-grade and dehydrated commercial-grade hydroxides. Some reduction in corrosion rates may be expected in these poorer-quality hydroxides.

METALLOGRAPHY

The specimen preparation of stainless steel is very similar to that of any other metal or alloy. Specimens which are too small to be handled conveniently can be mounted in bakelite. Rough polishing is done on silicon carbide papers.

Final polishing may be done either by mechanical or electrolytic means. When mechanical polishing is used, the abrasive powder can be levigated alumina and the polishing cloth silk or silk-velvet. Care must be taken to prevent any flowed metal from getting on the specimen surface. On etching, flowed metal can mask the microstructure of the specimen. The combination of etching, repolishing, and etching can be used to minimize flowed metal.

For electrolytic polishing the following electrolyte is used:

2 parts acetic anhydride
1 part perchloric acid
0.5 percent aluminum dissolved in the electrolytic
polishing of an aluminum specimen.

Iron is used as the cathode, and the specimen is the anode. An externally applied voltage of about 50 v is used with a current density of 4 to 6 amp/sq dm. Polishing time is about 4 to 5 min.

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*Reports of ANL, BMI, KAPL, and ORNL contain data on stainless steel corrosion under various conditions.

CHAPTER 1.19

Thorium and Its Alloys

J. R. Keeler

Thorium is a soft, silvery-white metal which prior to the MED project had been prepared only in small quantities of varying degrees of purity. With the advent of the atomic energy program, interest in thorium increased because this element is a potential source of the secondary nuclear fuel U^{233} , and the possibilities of "breeding" with thorium to increase the supply of fissionable material were recognized. The metal is available now in ton quantities at a cost of approximately \$15.00/lb, and its properties have been studied extensively.

ABUNDANCE AND AVAILABILITY

Although thorium is distributed widely over the earth's surface, being present in concentrations of approximately 12 ppm in the earth's crust, few economically workable deposits have been found. Deposits which contain significant amounts have been found in India, Brazil, Ceylon, Tasmania, Nigeria, the Ural Mountains, and the Scandinavian peninsula.

No large deposits are known in the United States. The principal domestic sources have been the beach sands of Oregon, small alluvial deposits in the Piedmont Area in North and South Carolina, and complex mineral deposits in Florida. Workable deposits have been found in Idaho, and production from this area is being expanded rapidly. The gold-dredging operations in Idaho and California are potential sources because of the scale of the dredging operation, and skyrocketing prices for monazite have increased the efforts to recover this ore.

In recent years, the principal source of monazite sand, which is the only significant ore, has been the deposits in India and Brazil. Large deposits have been developed recently in southwest Africa near the mouth of the Orange River; these deposits may become one of the principal sources of the ore. The sands consist essentially of the orthophosphates of the rare-earth metals together with smaller amounts of thorium and uranium. The sands usually are concentrated by ore-dressing methods until they contain from 57 to 60 percent of rare-earth oxides. A typical analysis of Brazilian concentrate is as follows:

ThO_2	6.5%
U_3O_8	0.17%
$(RE)_2O_3^*$	59.2%
P_2O_5	26.0%
TiO_2	1.75%
Fe_2O_3	0.51%
SiO_2	2.16%

*Rare-earth oxides.

EXTRACTION AND PURIFICATION

EXTRACTION

Several methods for the extraction of thorium compounds from monazite sand are available. The usual commercial method is to digest the sand with excess concentrated sulfuric acid. A thick paste results which is stirred gradually into additional water and allowed to settle. The solution contains the bulk of the thorium and rare earths, perhaps as phosphate complexes.

The thorium is separated either by partial neutralization to effect fractional precipitation of the thorium phosphate, or by a carbonate separation which is based on the fact that thorium carbonate is much more soluble in excess sodium carbonate than are the carbonates of the rare earths. An oxalate separation based on the solubility of thorium oxalate in an ammonium oxalate solution also may be used.

Digestion of the monazite sand with caustic soda and solvent extraction of the thorium has been carried out on a pilot-plant scale but has not yet been applied to commercial production. Solvent extraction of thorium after digesting the monazite sand with sulfuric acid also has been studied extensively.

Currently, commercial "mantle-grade" thorium nitrate is used as the starting material for the production of metal at the Ames Laboratory, the primary producer of metallic thorium.

The requirements for purity of the metal depend on the ultimate use. The removal of contaminants with large thermal-neutron-absorption cross section is necessary for thorium that is to be irradiated in order to obtain a favorable neutron economy. In general, however, this step is less important for thorium than for uranium, unless the thorium is to be irradiated in the high-flux section of the pile. Metal approaching this analysis can be made from unextracted commercial thorium nitrate.

Carbon, oxygen, and other elements with low-capture cross sections for thermal neutrons may not be seriously harmful. In fact, as indicated in subsequent sections, carbon in small amounts is a beneficial addition from the standpoint of improving the strength of the metal.

PREPARATION OF THE METAL

The preparation of metallic thorium in the pure state is particularly difficult because of its high melting point and its reactivity with hydrogen, oxygen, nitrogen, carbon, and other metals. Prior to the MED project, the metal was prepared in small quantities of varying degrees of purity by the reduction of its halides and oxide with alkali and alkaline-earth metals, by thermal decomposition of thorium compounds, and by the electrolysis of thorium compounds in fused salts. The production of thorium up to 1927 is summarized in Gmelin's *HANDBUCH DER ANORGANISCHEN CHEMIE*.

EARLY METHODS OF PRODUCING METAL

At the beginning of the MED project, the Westinghouse Electric Company was making thorium on a small scale by the reduction of thoria with calcium. This method, as developed by Marden and others at Westinghouse, produced powdered metal which was pressed and sintered into solid bars. The metal thus produced was quite ductile and easily worked. The principal impurity was oxygen, which was present in amounts of 0.15 to 0.17 percent.

BOMB REDUCTION

The preparation of thorium by the method used for the production of uranium, that is, the reduction of the fluoride by calcium, was investigated by Spedding, Wilhelm, et al., at Iowa State College and brought by that group to its present state of development.

IODIDE METHOD

Metal has been produced by the DeBoer iodide process which, on the basis of hardness and microstructure, appears to be of exceptional purity. Thorium tetraiodide, produced by the reaction of iodine on machined chips of bomb-reduced metal, is thermally decomposed on a heated filament. The entire process is carried out inside a sealed Vycor tube and has been limited thus far to approximately 300-gm batches.

The product is a loosely knit crystalline deposit which when arc melted in a helium atmosphere has a hardness of 35 Vickers. This hardness is roughly half that of as-cast bomb-reduced metal, and the microstructure of the melted button is practically free of inclusions. Analyses of bomb-reduced, iodide, and powder-process thorium are given in Table 1.19.1. The metallic impurities present in iodide thorium are approximately the same amounts as in the bomb-reduced metal, but the quantity of gaseous elements and carbon are greatly reduced.

Table 1.19.1 — Partial Analyses of Various Types of Thorium

Element	Concentration, ppm		
	Bomb-reduced	Iodide	Powder-process
O ₂	1600	<100	...
N ₂	200	<100	...
C	593	200	430
Al	<100	<100	<160
Si	<100	<100	100
Fe	<100	135	200
Be	144	<100	...

PHYSICAL AND CHEMICAL CONSTANTS

Table 1.19.2 lists the principal physical and chemical constants of thorium.

HEALTH HAZARDS

Thorium, like uranium, is an alpha emitter and the parent element of the radioactive thorium series. Considerable quantities of highly radioactive radon may be released in grinding the ores, and radioactive products also are released during the reduction and casting of the primary metal. The processed metal has a relatively low activity level and is handled without protective clothing or shielding. Competent medical authorities should be consulted regarding the handling of and tolerances for thorium.

MECHANICAL PROPERTIES

The mechanical properties of thorium are extremely sensitive to small quantities of impurities, and large differences are observed between the properties of iodide metal and bomb-reduced metal. Smaller variations are also found in the properties of individual billets. Since each billet represents a separate heat, there are slight differences in analy-

Table 1.19.2—Physical and Chemical Constants of Thorium

Density*, gm/cm ³	
Theoretical	11.71
Ames casting	11.55 – 11.63
Arc-melted iodide	11.66
Melting point, °C	1690 ± 10
Boiling point, °C	>3000
Heat of fusion, kcal/mole	4.6
Heat of vaporization, kcal/mole	130
Specific heat, cal/(mole)(°C)	
99.3°C	6.59
198.7°C	6.61
Entropy, cal/(mole)(°C)	
25°C	13.6 ± 0.8
Coefficient of thermal expansion, per °C × 10 ⁶	
30° to 100°C	11.5
30° to 500°C	11.9
30° to 1000°C	12.5
Thermal conductivity†, cal/(sec)(cm)(°C)	
100°C	0.090
650°C	.108
Electrical resistivity, μohm-cm	
20°C	18
Thorium is superconducting below 1.70°K	
Crystallography	
Crystal structure	Face-centered cubic
Lattice constant, a ₀ , Å	
26.2°C	5.0871 ± 0.0002
Atomic diameter	3.59
Coordination number	12
Allotropic transformation	None known to exist

*Gm/cm³ × 62.43 = lb/cu ft†Cal/(sec)(cm)(°C) × (2.419 × 10²) = Btu/(hr)(ft)(°F)

sis which are reflected in the properties of the metal. Figures 1.19.1 and 1.19.2 show the variation in tensile and impact strength of thirty-two bomb-reduced billets as cast, and Table 1.19.3 indicates the variation in mechanical properties of several wrought billets.

Available analytical data are insufficient to explain completely the effect of each element in the bomb-reduced metal, but the carbon content appears to be one of the principal factors affecting the mechanical properties.

The effect of carbon, oxygen, and nitrogen additions on the tensile strength of arc-melted iodide metal is indicated in Fig. 1.19.3. Oxygen and nitrogen have little effect on the strength of the metal, but carbon increases the strength markedly. (The properties of other alloys are discussed later in this chapter.) The metal also is sensitive to the strain rate, and significant differences in the mechanical properties can be obtained by varying the rate of application of the test load.

TENSILE AND COMPRESSIVE PROPERTIES

Typical room-temperature tensile properties of bomb-reduced billet are shown in Table 1.19.4. The properties of iodide metal and powder-process metal also are shown. In typical

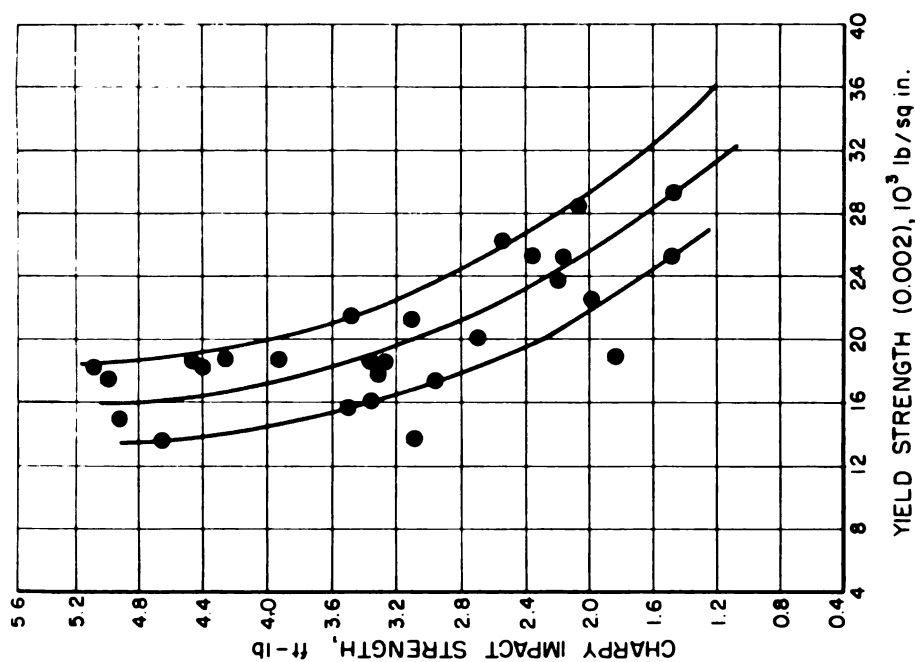


Fig. 1.19.2 — Variation of Charpy Impact Strength With Yield Strength for Twenty-seven Bomb-reduced Thorium Billets, As Cast. Reprinted from "Interim Report of an Investigation of the Properties of Thorium and Some of Its Alloys," G. C. Danielson, et al., ISC-200, Jan. 18, 1952.

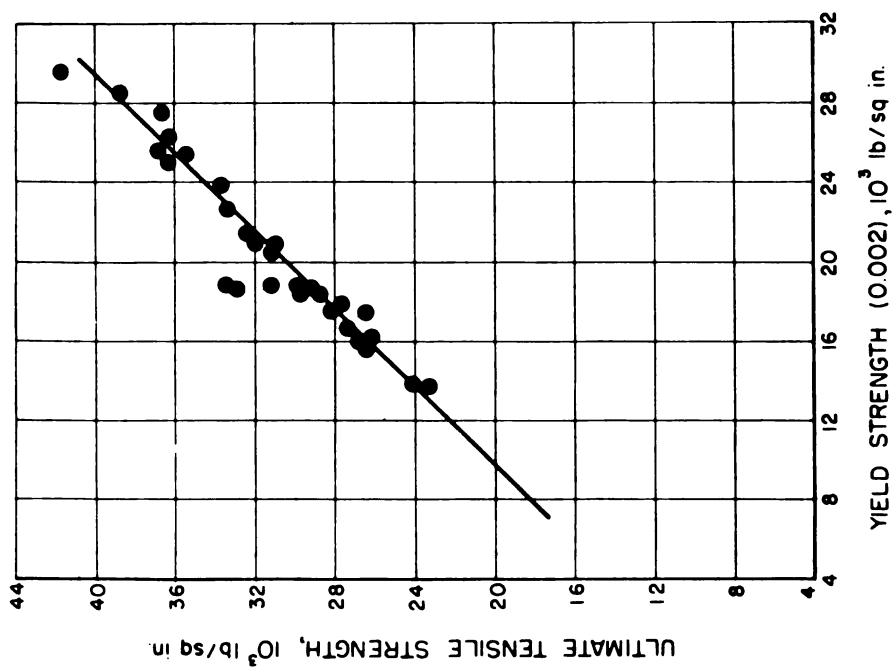


Fig. 1.19.1 — Variation of Tensile Strength With Yield Strength for Twenty-nine Bomb-reduced Thorium Billets, As Cast. Reprinted from "Interim Report of an Investigation of the Properties of Thorium and Some of Its Alloys," G. C. Danielson, et al., ISC-200, Jan. 18, 1952.

Table 1.19.3 — Variation in Mechanical Properties of Wrought Bomb-reduced Thorium Billets

Material	Condition	Chemical composition, wt-%						Yield strength (0.2% offset), lb/sq in.	Tensile strength, lb/sq in.	Elongation (1.4 in. gauge length), %	Reduction of area, %	Proportional limit, lb/sq in.	Impact strength (Charpy V-notch), ft-lb
		C	Al	Be	N	Si	Total impurities						
Remelted chips	*	0.064	0.015	0.020	0.025	0.030	0.18	31,000	74,300	49.5	69.2	18,700	16.5
	†							28,500	71,300	52.7	70.1	22,400	18.3
Remelted chips	*	.078	.030	.023	.038	.030	.22	37,700	44,300	48.6	65.2	25,300	9.7
	†							29,700	38,800	49.3	64.6	21,300	12.8
	‡							53,500	59,200	18.6	51.5	30,500	3.5
	§							30,500	39,000	48.2	58.0	23,700	12.8
Virgin metal	*	.033	<.01	.012	<.01	.030	.12	19,700	28,700	53.1	75.4	11,900	39.8
	†							19,300	27,700	53.6	75.8	12,500	38.3
	‡							39,900	41,900	18.8	64.0	23,900	8.8
Virgin metal	*	.067	<.01	.010	.013	.030	.16	23,900	32,500	55.4	72.2	16,400	29.0
	†							23,900	31,500	58.9	73.4	17,800	29.0
	‡							40,900	43,300	23.2	63.2	26,000	7.8
	§							25,600	31,100	57.9	69.7	20,700	28.6
Virgin metal	*	.050	.015	.018	<.01	.030	.15	17,200	27,500	46.5	75.6	10,300	40.1
	†							17,300	25,500	55.4	76.3	13,200	34.2
	‡							36,500	39,500	18.8	66.3	21,800	11.6
	§							18,500	26,100	59.3	74.9	12,400	29.8
Virgin metal	*	.084	<.01	.018	.010	.030	.17	22,400	30,600	54.5	76.1	15,600	32.9
	†							22,200	29,900	51.8	75.6	16,000	30.0
	‡							41,900	44,400	19.0	63.7	26,400	8.7
	§							24,100	29,700	62.5	71.5	19,400	24.0

* As extruded (1740°F, 23:1 reduction)

† Extruded (1740°F, 23:1 reduction) and annealed 30 min at 1380°F

‡ Extruded (1740°F, 4.5:1 reduction) and cold rolled 37.5%

§ As in (†) and annealed 30 min at 1380°F

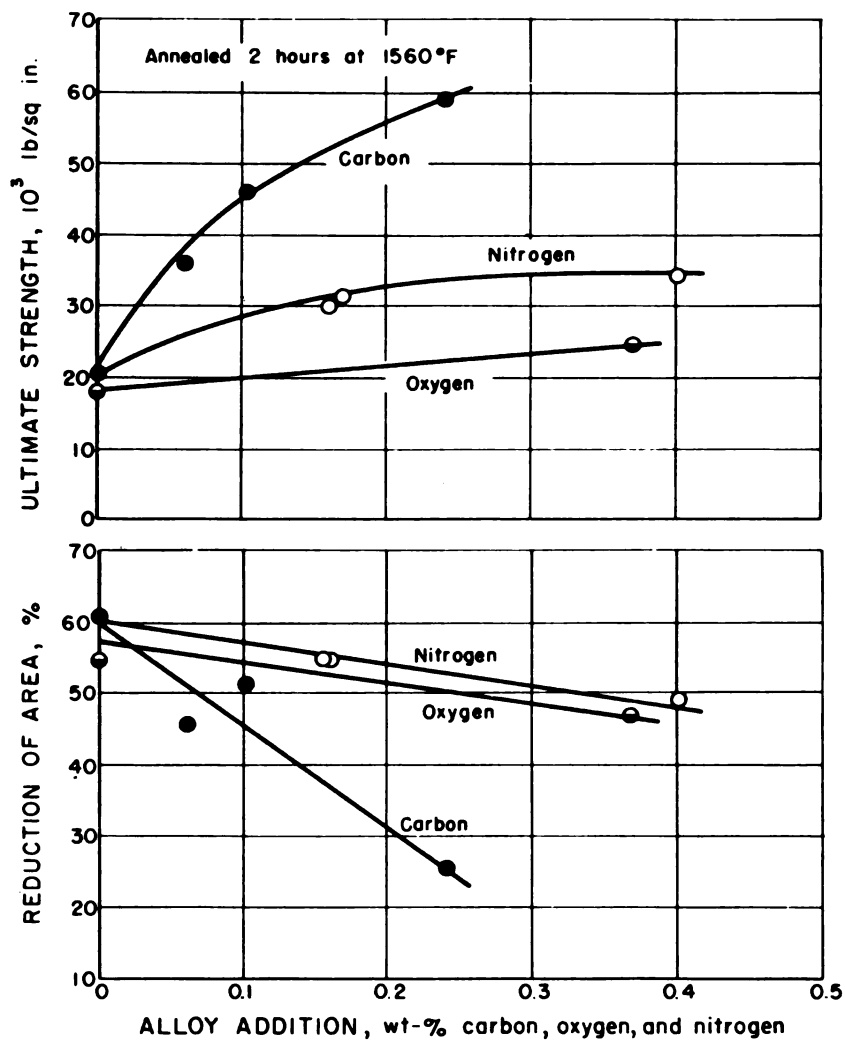


Fig. 1.19.3—The Effect of Carbon, Oxygen, and Nitrogen on the Tensile Strength of Iodide Thorium. Submitted by Battelle Memorial Institute, July 1, 1952.

Table 1.19.4—Typical Room-temperature Tensile Properties of Bomb-reduced, Powder-process, and Iodide Thorium

Type metal	Typical analysis, ppm								Strain rate, in./in. (min)	Fabrication history	Proportional limit, lb/sq in.	Yield strength, (0.2% offset), lb/sq in.	Ultimate strength, lb/sq in.	Reduction of area, %	Elongation, %	Young's modulus, 10 ⁶ lb/sq in.		
	O	H	N	C	Al	Si	Be	Fe									Ni	Cr
Bomb-reduced	1,500	<100	<100	700	150	110	225	250—350	—100	200	0.05	*	19,700	25,600	31,200	73	63	10
Powder-process	1,500	430	<160	100	0.4	200	...	<100	.05	†	18,300	...	28,400	6.9	9	...
Iodide	<100	<100	<100	200	100—1,000	<100	...	135	<100	<100	...	‡	22,860	~95	Broke outside gauge marks	...

* Forged and hot rolled to $1\frac{1}{4}$ -in. diam; cold rolled to $\frac{13}{16}$ -in. diam; annealed 1 hr at 1470°F; standard 0.505 tensile† Annealed $\frac{1}{2}$ hr at 1380°F; standard 0.505 tensile‡ Arc melted, cold rolled and machined to 0.375 tensile specimen; annealed $\frac{1}{2}$ hr at 1380°F

stress-strain curves for bomb-reduced metal, a yield-point phenomenon is observed, particularly at high strain rates. As in the case of low-carbon steel, the yield point is removed by cold work but returns when the metal is aged at elevated temperatures approaching the recrystallization temperature.

Increasing the strain rate from 0.003 to 0.016 in./(in.)(min) increases the 0.2-percent-offset yield strength from 24,500 to 32,300 lb/sq in. and the ultimate strength from 35,600 to 37,300 lb/sq in. At higher strain rates, the yield strength approaches and may exceed the ultimate strength. Table 1.19.5 shows the effect of strain rates up to 39.6 in./(in.)(min) on sheet tensile specimens.

Table 1.19.5—The Effect of Cold Work on the Room-temperature Tensile Properties of Bomb-reduced Thorium

Amount of cold work, %	Test condition	Test direction	Strain rate, in./(in.)(min)	Proportional limit, lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Ultimate strength, lb/sq in.	Reduction of area, %	Elongation, %
25	As rolled	Perpendicular to RD	0.007	25,500	45,500	46,800	36	...
25	As rolled	Parallel to RD	.007	26,500	42,500	43,600	33.9	...
25	Annealed*	Perpendicular to RD	.007	17,300	24,500	33,850	41.2	...
25	Annealed*	Parallel to RD	.007	15,000	24,700	33,200	48.5	...
50	As rolled	Parallel to RD	.007	27,500	42,900	44,200	28	6.3
50	Annealed*	Parallel to RD	.007	20,500	23,000	32,500	50	26
50	Annealed*	Perpendicular to RD	.007	20,100	23,100	32,600	49.0	26
50	Annealed*	Perpendicular to RD	39.6†	...	47,000	44,000	55.0	37
50	Annealed*	Parallel to RD	6†	...	37,000	37,200	43	35
50	Annealed*	Parallel to RD	39.6†	...	47,000	44,000	43.0	35

*Annealed 3 hr at 1350°F; grain size 0.010 mm

†At these strain rates, a yield phenomenon was noticed

Table 1.19.6—Compression Properties of Hot-rolled and Annealed Bomb-reduced Thorium

Temperature, °F	Atmosphere	Strain rate, in./(in.)(min)	Proportional limit, lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Young's modulus, 10 ⁶ lb/sq in.	Poisson's ratio
75	Air	0.005	17,000*	23,900	9.7 ± 0.2	0.25 ± 0.03
75	Air	.01	15,000*	26,200	9.7 ± 0.2	0.27 ± 0.01
75	Air	.01	18,000*	30,500	9.7	...
75	Air	.025	15,000*	26,000	10.0 ± 0.2	...
570	Argon	.01	9,200†	13,800	9.0 ± 0.2	...
570	Argon	.025	12,000†	17,000	8.9 ± 0.2	...

*Sensitivity of strain measurement was 5 μ in./in.

†Sensitivity of strain measurement was 60 μ in./in.

The effect of cold work on the tensile properties is also shown in Table 1.19.5. A 25-percent reduction in area by cold rolling nearly doubles the yield strength of the annealed strip and increases the ultimate strength by 30 to 40 percent. Increasing the amount of reduction to 50 percent, however, causes no significant additional increase in tensile properties. The directional properties in cold-rolled sheet are not pronounced. The strength perpendicular to the rolling direction is slightly greater than that parallel to the rolling direction, but the difference is less than 10 percent in sheet cold rolled to 25-percent reduction.

The compressive properties are shown in Table 1.19.6. The yield strength on compression is nearly the same as in tension and is also sensitive to the strain rate. Compression properties at 570°F are shown also. At room temperature, Poisson's ratio averages 0.265 in both tension and compression.

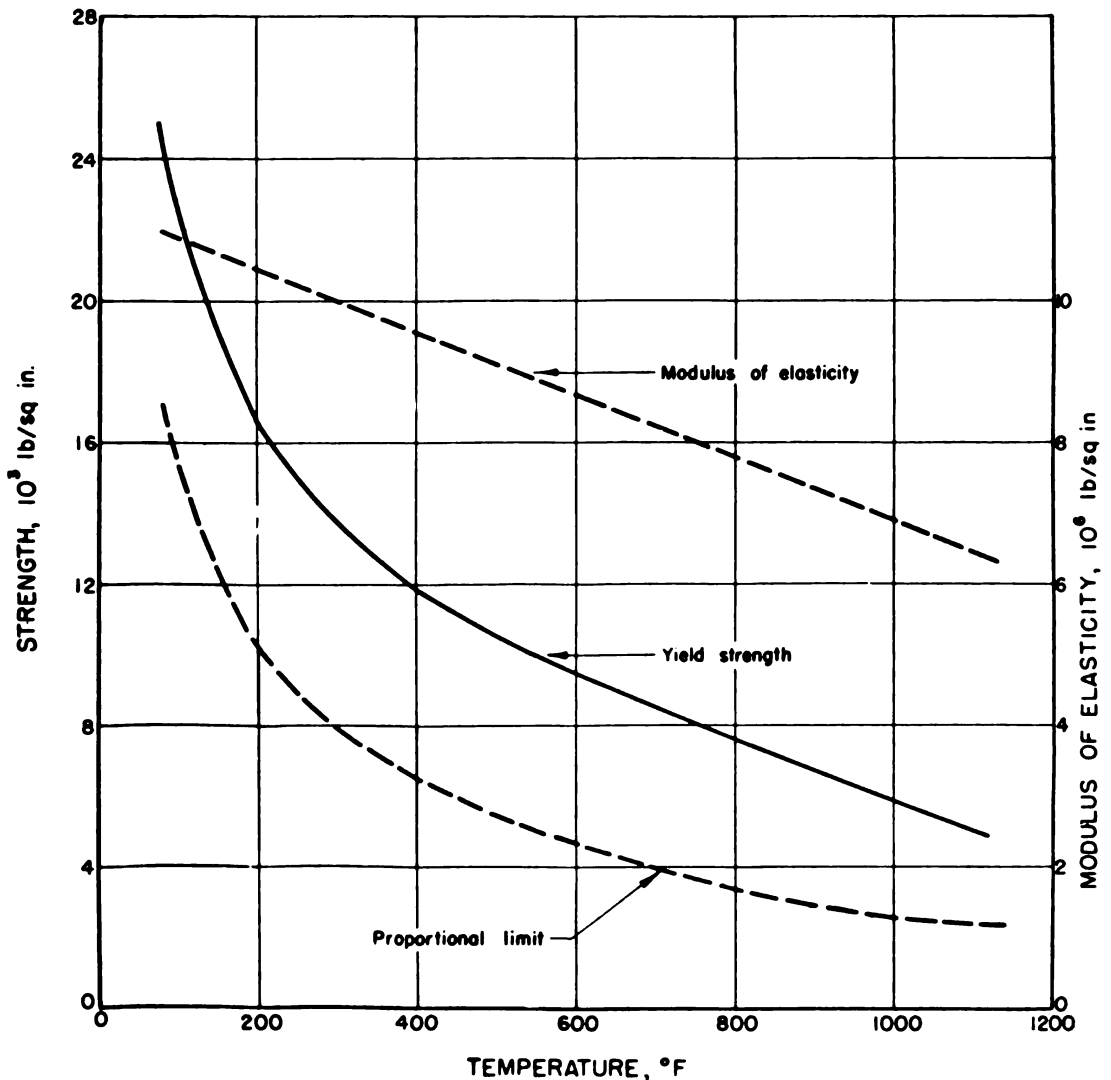


Fig. 1.19.4—The Tensile Properties of As-cast Bomb-reduced Thorium. Reprinted from "Progress Report of an Investigation of the Properties of Thorium and Some of Its Alloys," AL-24, G. C. Danielson, et al., July 1, 1951.

The strength of thorium decreases rapidly at elevated temperatures. Figures 1.19.4 and 1.19.5 show the tensile properties of a cast bomb-reduced billet and of a wrought bomb-reduced billet at temperatures up to 1100°F and 900°F, respectively.

On wrought material, the 0.2-percent yield strength decreases from 27,000 lb/sq in. at room temperature to 12,500 at 390°F and 9,500 lb/sq in. at 930°F. The effect on the ultimate strength is somewhat less pronounced; it decreases from 37,500 lb/sq in. at room temperature to 17,400 at 930°F. The modulus of elasticity shows a corresponding decrease from 10×10^6 lb/sq in. at room temperature to 7.1×10^6 lb/sq in. at 930°F.

IMPACT STRENGTH

The variation in impact strength of a large number of cast bomb-reduced thorium billets is shown in Fig. 1.19.2. The Charpy impact strength of the cast metal varies from 1.5 to 10.5, probably depending on the impurity content of each billet. The correlation between analysis and mechanical properties has not been established fully, but, as indicated in

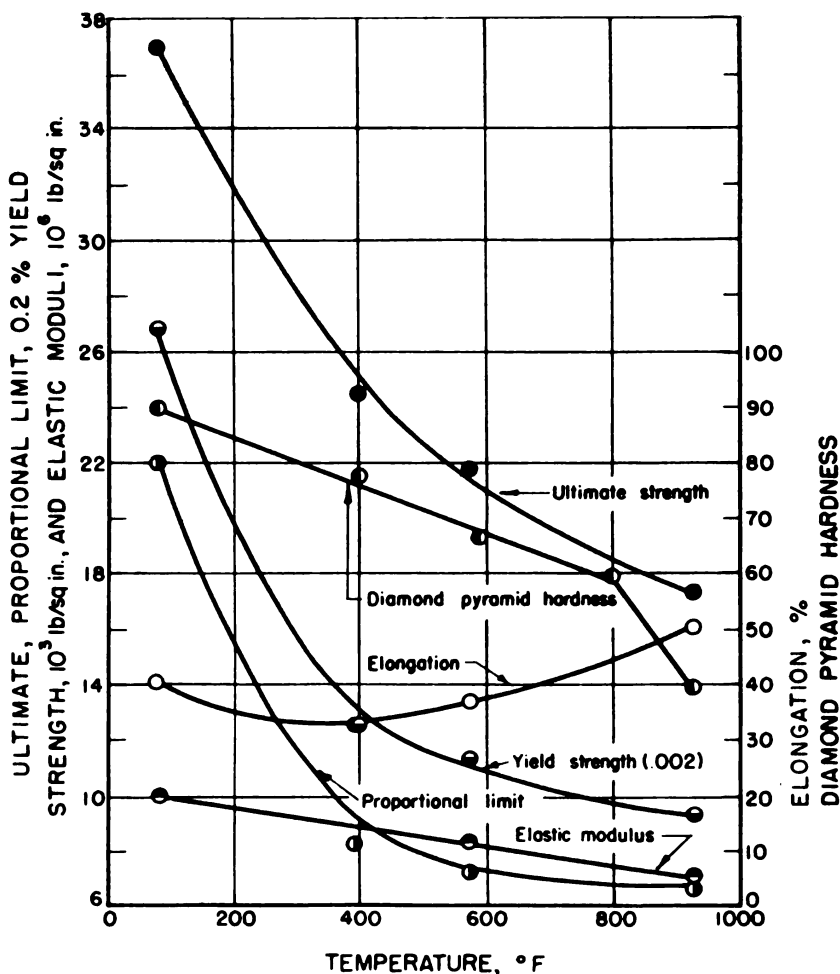


Fig. 1.19.5—The Tensile Properties of Hot-rolled and Annealed Bomb-reduced Thorium. Submitted by Battelle Memorial Institute, July 1, 1952. Strain rate 0.007 min^{-1} .

Fig. 1.19.6, the impact strength of several billets appears to decrease with increasing carbon and beryllium content.

Wrought bomb-reduced thorium exhibits a transition from brittle to ductile behavior in the temperature range 210° to 390°F. Figure 1.19.7 shows the Charpy V-notch values obtained on wrought bomb-reduced metal.

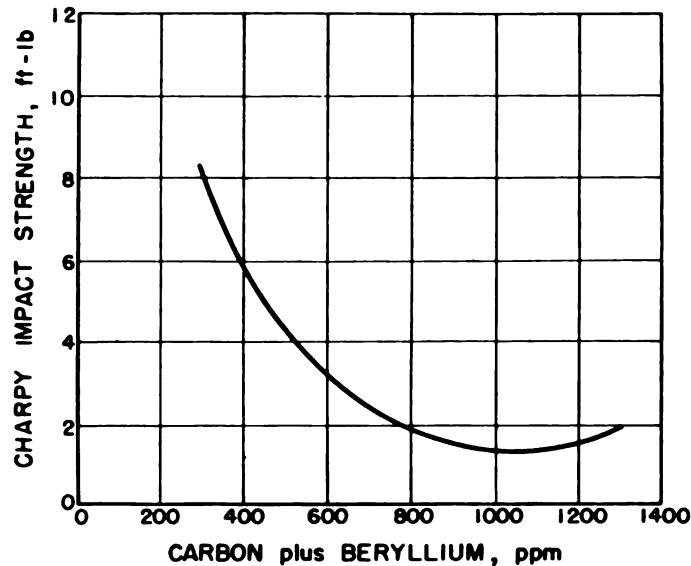


Fig. 1.19.6—The Variation of Room-temperature Impact Strength of Cast Bomb-reduced Thorium With Carbon Plus Beryllium Content. Adapted from "Interim Report of an Investigation of the Properties of Thorium and Some of Its Alloys," G. C. Danielson, et al., ISC-200, Jan. 18, 1952.

SHEAR MODULUS

The variation of the dynamic shear modulus and internal friction as determined by the torsional vibration technique (0.28 to 0.21 cycles/sec) is shown in Fig. 1.19.8. At room temperature, the dynamic shear modulus of annealed material is 4.62×10^6 lb/sq in. This modulus decreases gradually with increasing temperature to 3.8 at 570°F and then drops off sharply at higher temperature.

FATIGUE

As in the case of creep properties, data on the fatigue properties of thorium are limited to preliminary exploratory-type tests. Rotating-beam type tests at room temperature on a cast billet give an endurance limit of 12,000 to 12,500 lb/sq in. for 5×10^8 cycles. Cold rolling increases this limit to 15,000 lb/sq in.

Bending-fatigue tests on hot-rolled and annealed sheet specimens of the design indicated in Fig. 1.19.9 give an endurance limit (10^7 cycles) of 22,000 lb/sq in. for unnotched samples and 18,000 lb/sq in. for notched samples. The S-N diagram obtained on these sheet specimens is given in Fig. 1.19.10.

Axial-load fatigue tests indicate that the endurance limit on the basis of 10^7 cycles is approximately 15,000 lb/sq in. for a load ratio, $R = -1.0$, and is about the same at $R = 0.02$.

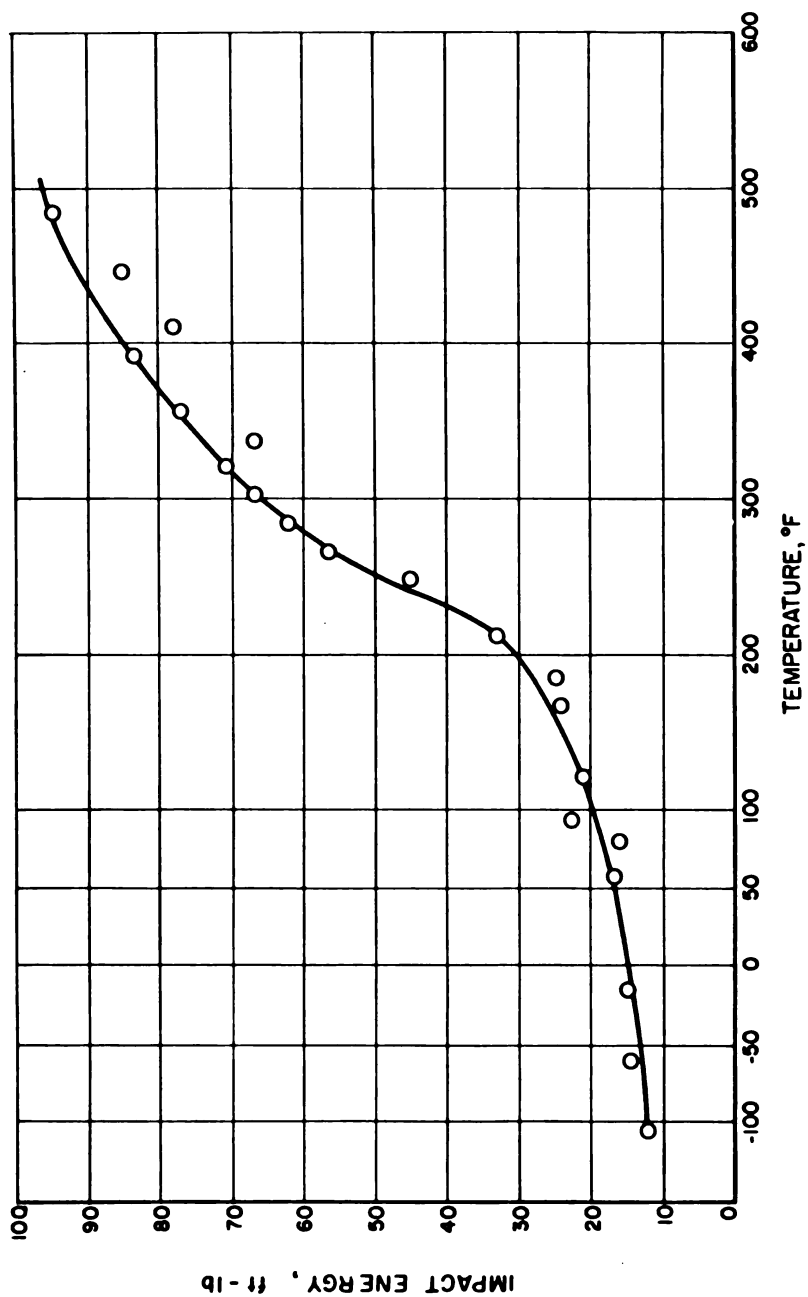


Fig. 1.19.7 — The Effect of Temperature on the Impact Strength of Hot-rolled and Annealed Bomb-reduced Thorium; Charpy Specimen. Submitted by Battelle Memorial Institute, July 1, 1952.

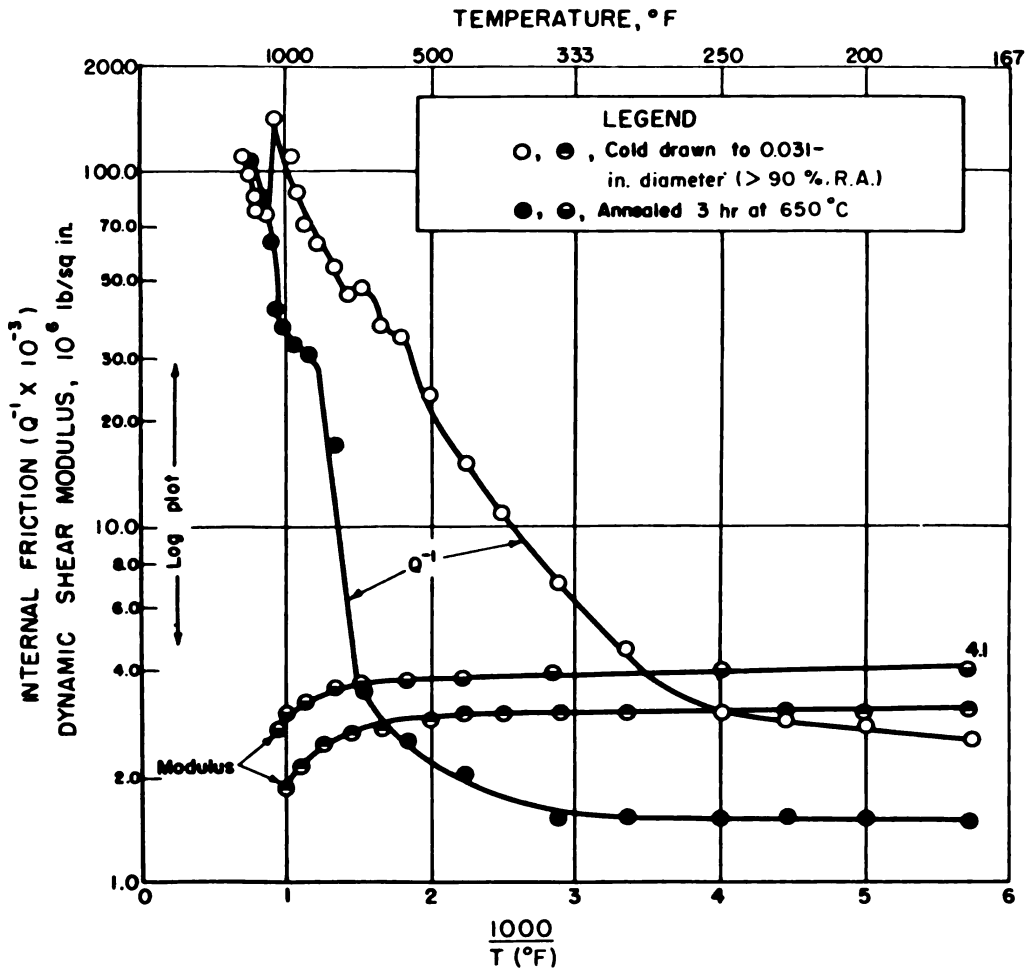
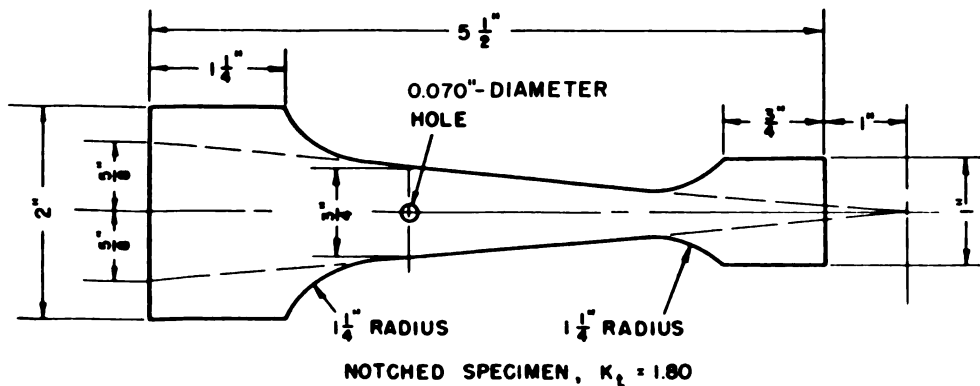


Fig. 1.19.8—The Effect of Temperature on the Dynamic Shear Modulus and Internal Friction of Bomb-reduced Thorium Wire. Submitted by Battelle Memorial Institute, July 1, 1952.



NOTE: UNNOTCHED SPECIMEN DOES NOT HAVE THE 0.070"- DIAMETER HOLE

Fig. 1.19.9—Constant Stress, Unnotched and Notched Plate-bending Fatigue Test Specimens. Submitted by Battelle Memorial Institute, July 1, 1952.

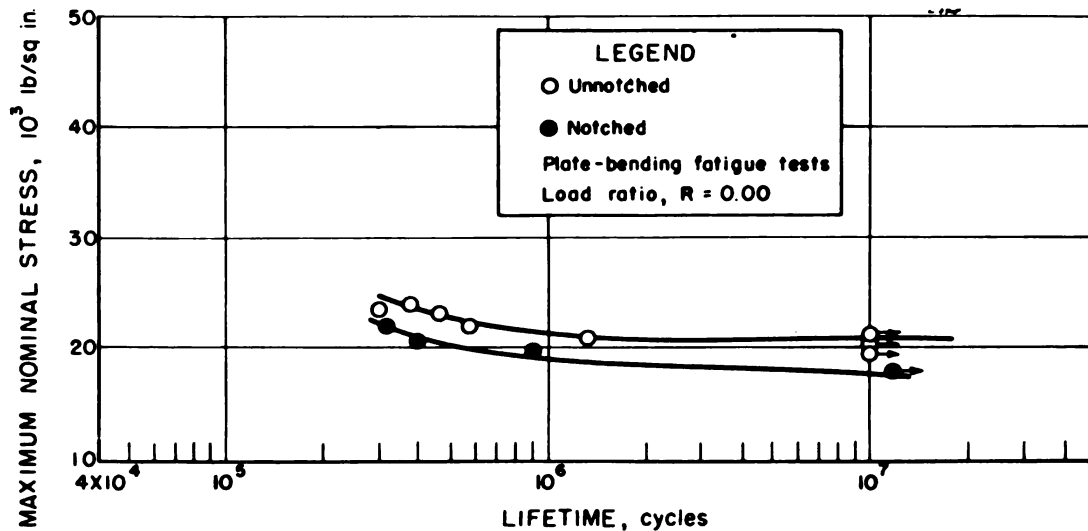


Fig. 1.19.10—S-N Curves for Unnotched and Notched Thorium Sheet Specimens. Submitted by Battelle Memorial Institute, July 1, 1952.

CREEP

Exploratory creep tests have been run on thorium, but the amount of information available is limited. At room temperature, a cast specimen loaded at 20,000 lb/sq in. had a constant creep rate of 2.67 $\mu\text{in.}/(\text{in.})(\text{hr})$ for some time, but the creep rate then decreased to virtually zero. This specimen was reloaded to 25,000 lb/sq in., and a creep rate of about 10.9 $\mu\text{in.}/(\text{in.})(\text{hr})$ was observed over a period of 3 months.

The effect of temperature on the creep strength of bomb-reduced thorium sheet, cold rolled 33 percent and annealed 3 hr at 1300°F, is shown in Table 1.19.7. A typical creep curve at 600°F is shown in Fig. 1.19.11.

WORK-HARDENING CHARACTERISTICS

Thorium work hardens rapidly when subjected to cold working. The increase in hardness is small however, and thorium can therefore be cold worked to quite high reductions without intermediate anneals.

Table 1.19.7 — Creep Properties of Bomb-reduced Thorium*

Temperature, °F	Stress, lb/sq in.	Time, hr	Total deformation, %	Minimum creep rate, %/hr
200	20,000	1660	15.4	0.002†
400	14,000	1500	1.55	Nil
600	10,000	1300	1.4	0.0001

*A typical creep curve is shown in Fig. 1.19.11

†Third-stage creep started after ~1100 hr

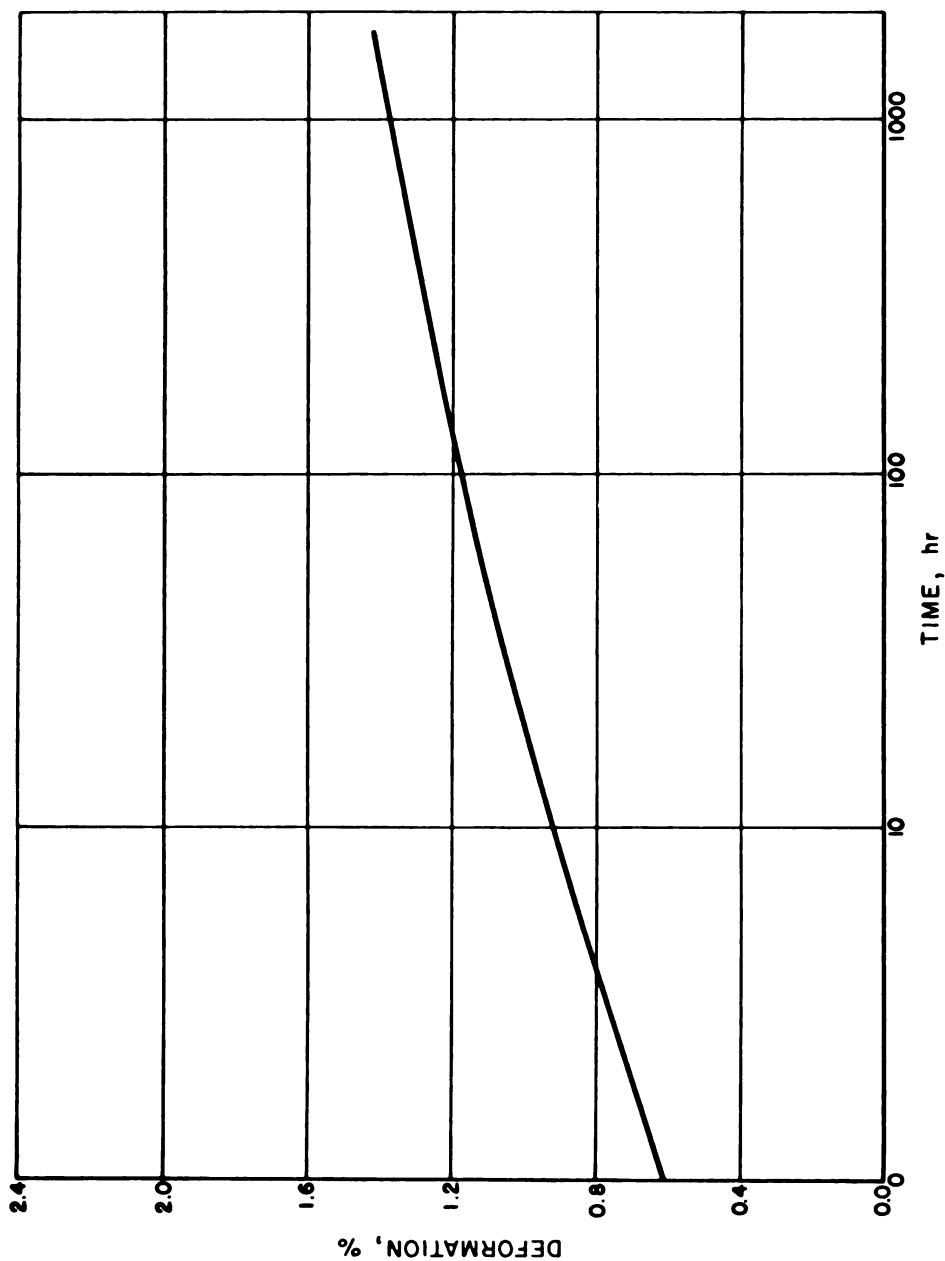


Fig. 1.19.11 — Creep of Cold-rolled Thorium Sheet Annealed 3 Hours at 1350°F in an Argon Atmosphere. Submitted by Battelle Memorial Institute, July 1, 1952. Test conducted at 600°F at 10,000 lb/sq in. in a vacuum.

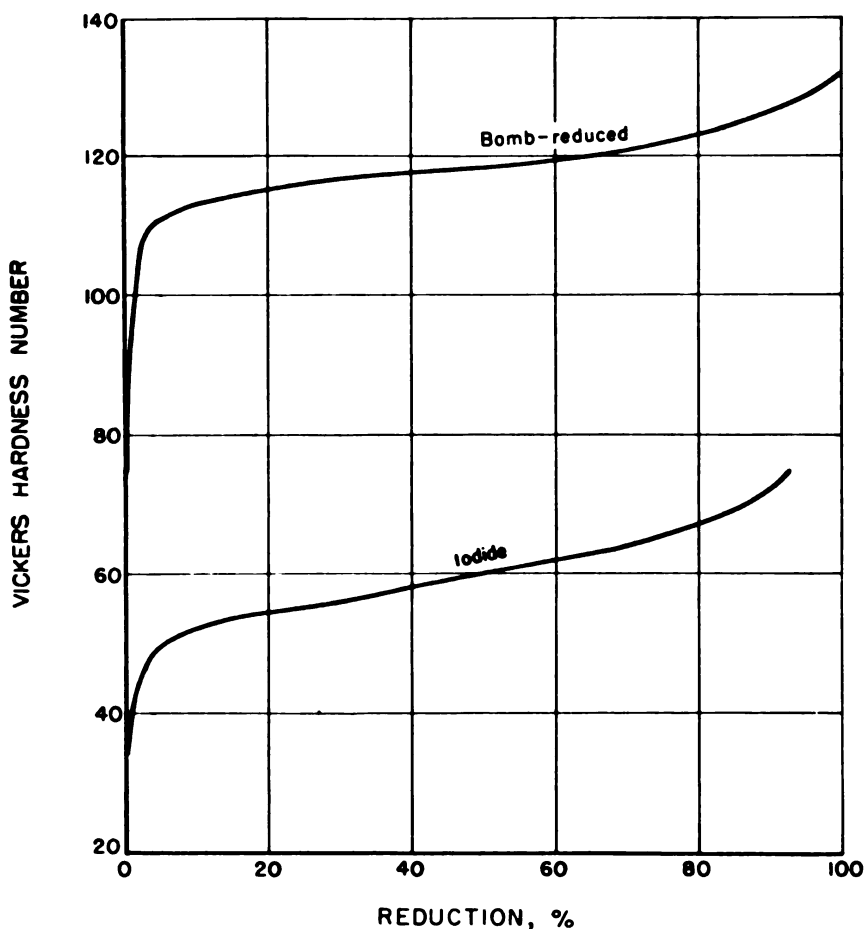


Fig. 1.19.12 — The Effect of Cold Rolling on the Hardness of Bomb-reduced and Iodide Thorium. Reprinted from "Quarterly Progress Report for Period Ending January 31, 1951," E. C. Miller and W. H. Bridges, editors, ORNL-987, June 7, 1951.

The increase in hardness of iodide and bomb-reduced thorium upon cold working is shown in Fig. 1.19.12.

MELTING AND CASTING

Because of its high melting point and reactivity, thorium is a difficult metal to melt. It is necessary to melt it in a vacuum or inert atmosphere to avoid contamination with oxygen and nitrogen. The metal usually is heated by induction, but small melts have been made in arc furnaces.

Crucibles from a number of refractories have been investigated and several have good resistance to attack of the molten metal.

FORMING AND FABRICATION

The mechanical-working characteristics of bomb-reduced thorium is generally good. The metal is soft and ductile when hot and can be worked by most of the standard metal-working procedures with only a few special precautions. An inert atmosphere or protective jacket is necessary when the metal is heated for hot working. There is no brittle temperature range, although castings have a tendency to crack when cold worked. After the cast structure has been broken up, the metal can be fabricated at room temperature. The various metalworking processes are discussed in the following sections.

EXTRUSION

Thorium can be extruded at reasonable pressures at temperatures in the range 900° to 1830°F. The metal generally is jacketed with copper or iron to protect the surface and to lubricate the die, but it also can be extruded bare. Higher pressures are required to extrude unjacketed metal, and some die erosion occurs at the higher extrusion temperatures. Good surface quality can be obtained in either case under proper conditions.

Thorium and copper react to form a pyrophoric compound at temperatures of 1650°F and above, and some reaction occurs at temperatures as low as 1470°F. This reaction can be prevented by plating the interior of the copper can with chromium or by applying a BeO wash to the thorium prior to canning.

DEFORMATION AND RECRYSTALLIZATION TEXTURES IN EXTRUDED THORIUM

At low extrusion rates at 1560°F, thorium does not recrystallize, and the deformation texture in rods is similar to that of other face-centered-cubic metals, i.e., with a major texture of [111] and a minor [100] texture. At high extrusion rates, the metal recrystallizes and a single [114] texture is produced. Intermediate extrusion rates yield partially recrystallized structures with a major [114] texture and a minor [100] texture.

FORGING

Thorium forges readily at temperatures of 1380° to 1470°F. The metal is notch sensitive, and defects in the ends of billets tend to produce cracks during the forging operation.

ROLLING

After the cast structure has been broken up, thorium can be rolled over a wide range of temperatures. Standard open-pass rolls, designed for rolling steel rods, produce satisfactory thorium rods.

Aluminum in the metal makes it hot short, but nitrogen in amounts up to approximately 1000 ppm does not affect the hot-working characteristics. A billet containing 3500 ppm of aluminum could not be rolled, but a heat containing 235 ppm of aluminum and 885 ppm of nitrogen rolled at 1560°F without difficulty. A hot-rolled $\frac{3}{4}$ -in. diameter rod of this heat was subsequently cold rolled to 0.47-in. diameter in hand-rounding rolls without cracking.

The "as-cast" metal can be cold rolled but develops edge cracks after reductions of approximately 10 percent. Hot working greatly improves the cold-rolling properties of the metal. Reductions of 80 to 90 percent can be made on previously hot-rolled sheet without serious edge cracking, and one-mil foil can be rolled from 0.020-in. thick hot-rolled sheet without intermediate anneals. Hot-rolled bar stock can be rolled from 0.875-in. diameter to 0.427-in. diameter in hand-rounding rolls without evidence of cracking.

An indication of the hot- and cold-working characteristics of a large number of alloys has been obtained by forging and rolling small (approximately 38-gm) arc-melted buttons

of various alloys. Binary alloys containing 1 and 5 atomic-percent additions of most of the elements were made. Of these, the 5-percent alloys of aluminum, silver, gold, bismuth, beryllium, cobalt, iron, gallium, germanium, nickel, oxygen, lead, platinum, palladium, antimony, tin, and thallium could not be hot worked at 1290°F. Alloys containing cobalt, palladium, platinum, and antimony could not be hot worked at the 2.5-atomic-percent level. All of the alloys which could be hot rolled also could be cold rolled to 50-percent reduction.

Induction-melted alloys containing up to 6 weight-percent of titanium, zirconium, and niobium are ductile, and the castings can be cold rolled to 75-percent reduction without cracking. All of these elements reduce the as-cast hardness markedly.

The effects of oxygen and carbon on the general fabricating characteristics have not been specifically investigated. However, powder-process metal which contains 0.15 to 0.17 percent oxygen is readily fabricated both hot and cold, and remelted bomb-reduced metal, containing 0.21 percent carbon, is forged and rolled without difficulty.

SWAGING

The swaging of small-diameter rod and wire is feasible in dies designed for mild steel. Rod $\frac{3}{8}$ in. in diameter has been swaged to 0.062-in. wire without intermediate anneals. Large-diameter rods, $\frac{3}{4}$ - to 1-in. diameter, tend to seize in the swaging dies, and special lubrication is required in this size range.

WIRE DRAWING

The tendency of the metal to seize to steel and Carboloy dies is particularly evident in wire drawing. None of the commercially available lubricants prevent seizure, and early attempts to draw wire were unsuccessful.

A lubricant consisting of 100 cm³ of thinned (3:1) Duco lacquer (No. 246-2048), 30 gm of Molykote (molybdenum disulfide), and 10 gm of fumed lead and zinc oxides prevents seizure of the thorium, and wire down to 0.045 in. is drawn from a $\frac{1}{4}$ -in. hot-rolled rod without intermediate anneals. Pointing is accomplished by swaging, and reductions of one B-and-S gauge number per pass are made. The wire is recoated with lubricant after every second pass.

Thorium wire down to 0.003 in. is made from arc-melted iodide metal by jacketing a $\frac{1}{4}$ -in. rod in a copper tube and drawing the composite. This wire is pointed by swaging and, in the smaller sizes, by pickling in nitric acid. The copper acts as a lubricant and is stripped from the wire in nitric acid when the desired size is reached. Thorium wire 0.008 in. in diameter is also made from bomb-reduced metal by this technique.

TUBE DRAWING

Small-diameter, thin-walled tubing can be drawn on mandrels from drilled bar stock or from extruded tubes with the aid of a special proprietary lubricant.

POWDER-METALLURGY TECHNIQUES

Powder-metallurgy methods have not been used extensively on thorium except in the production of metal by the powder-process. In this process, the metal powder obtained by the reduction of the oxide with calcium is compressed at 20 tons/sq in. and sintered in vacuum or in an inert atmosphere at approximately 2550°F. The resulting metal has good ductility, and the properties are, in general, similar to those of bomb-reduced metal. Table 1.19.1 shows a typical analysis of the powder-process metal.

Thorium powder can also be obtained from the massive metal by forming the hydride and subsequently reducing this hydride to metal by heating in a vacuum.

JOINING

The welding characteristics of thorium are erratic, probably as a result of variations in the metal purity or the welding conditions. The metal has a tendency to crack when welded by the shielded-tungsten arc process, but sound, single-pass welds have been made in $\frac{1}{8}$ -in.-thick hot-rolled sheet by this method. These welds have good ductility and tensile properties, but cracking invariably results when a second pass is made over the weld with the arc. Alloying with 2.5 atomic-percent of molybdenum, tungsten, or columbium improves the welding characteristics of the metal.

Spot welds can be made in $\frac{1}{16}$ -in.-thick sheet, but with $\frac{1}{8}$ -in.-thick sheet there is a tendency to crack around the weld nugget.

Resistance butt welds and flash welds have been made, but no data on the properties of these welds have been obtained.

Efforts to furnace-braze thorium with various commercial brazing alloys were unsuccessful because the alloys failed to wet the thorium surface. Silver-soldered joints have been made, but the joints were brittle.

MACHINING

The machining characteristics of thorium are comparable to those of mild steel. The metal can be turned with high-speed tools at lathe speeds of 150 to 175 ft/min. Coolants are desirable, but dry turning is practical.

The scale resulting from hot working is hard and dulls the cutting edge of tools much more rapidly than the clean metal. The surface of castings may be pyrophoric and must be machined slowly to avoid combustion of the chips.

Surface grinding produces a smooth, highly reflecting surface, which darkens on standing in air. The grinding wheels, however, tend to become loaded with metal. Shaping and milling operations are also practical.

HEAT TREATMENT

The impurities in thorium appear to be more soluble in the metal at elevated temperatures, and increases in hardness result when samples are quenched from temperatures above 1100°F. Figure 1.19.13 illustrates this effect on several samples of bomb-reduced thorium. The quenched samples contained fewer inclusions than furnace-cooled material and thermal-analyses curves also indicate a precipitation phenomenon in the 1200° to 1380°F temperature range.

RECRYSTALLIZATION

Isothermal-recrystallization curves at temperatures between 930° and 1110°F are shown in Fig. 1.19.14 for bomb-reduced thorium cold rolled to 80-percent reduction. The effect of the amount of cold work on the rate of recrystallization of this same metal is shown in Fig. 1.19.15. The amount of recrystallization, assuming that the hardness is directly proportional to the amount of recrystallization, is shown in Fig. 1.19.16. On the basis of these data, the activation energy for recrystallization of these samples was 41,900 cal/mole.

Iodide thorium has a higher recrystallization temperature than the bomb-reduced metal and shows only slight softening in 1 hr at 930°F. Figure 1.19.17 shows the effect of cold work on the recrystallization of iodide metal.

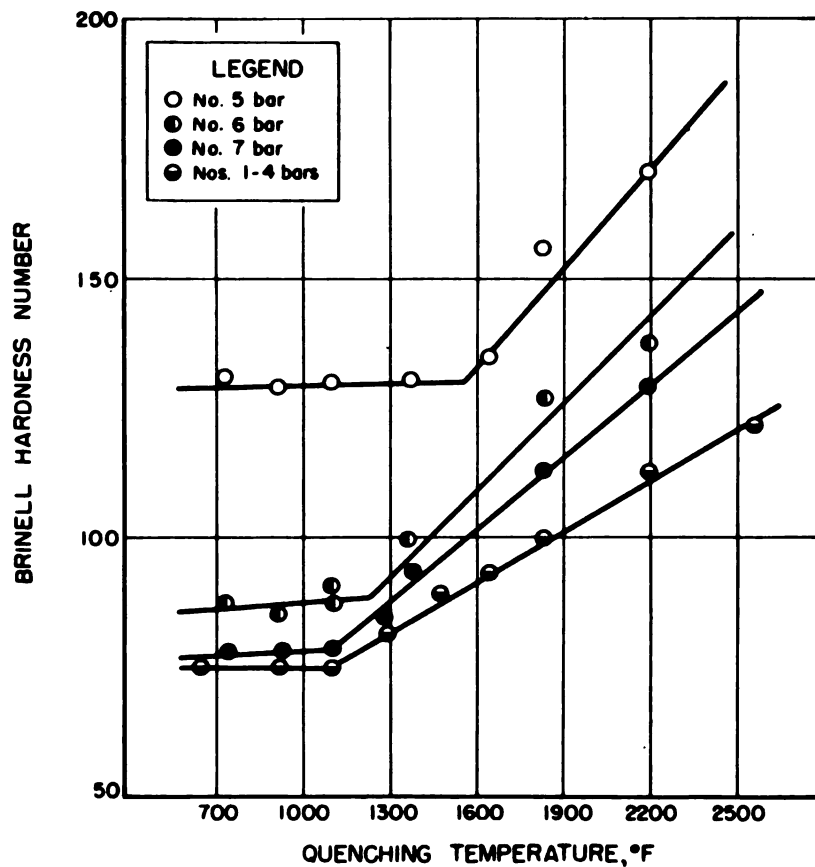


Fig. 1.19.13—Hardness of Thorium Bars Water-quenched after 2 hr at Temperature. Reprinted from "Some Aspects of the Recrystallization of Thorium," L. R. Jackson and W. W. Beaver, *J. of Met. and Cer.*, No. 4, Sept. 1949.

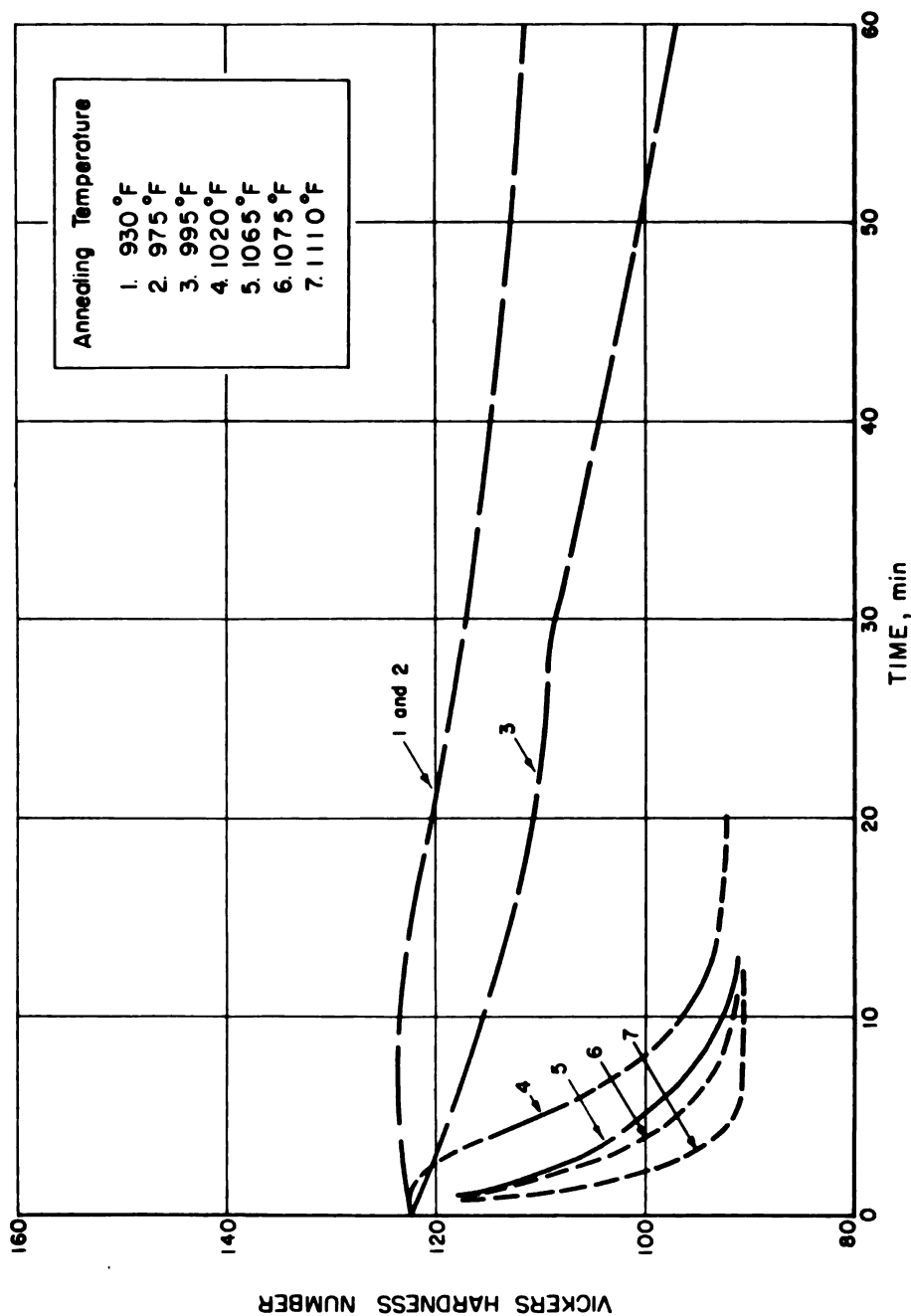


Fig. 1.19.14— Isothermal-recrystallization Curves for Bomb-reduced Thorium Sheet Cold Worked 80 Percent. Reprinted from "Quarterly Progress Report for Period Ending January 31, 1961," E. C. Miller and W. H. Bridges, editors, ORNL-987, June 7, 1961.

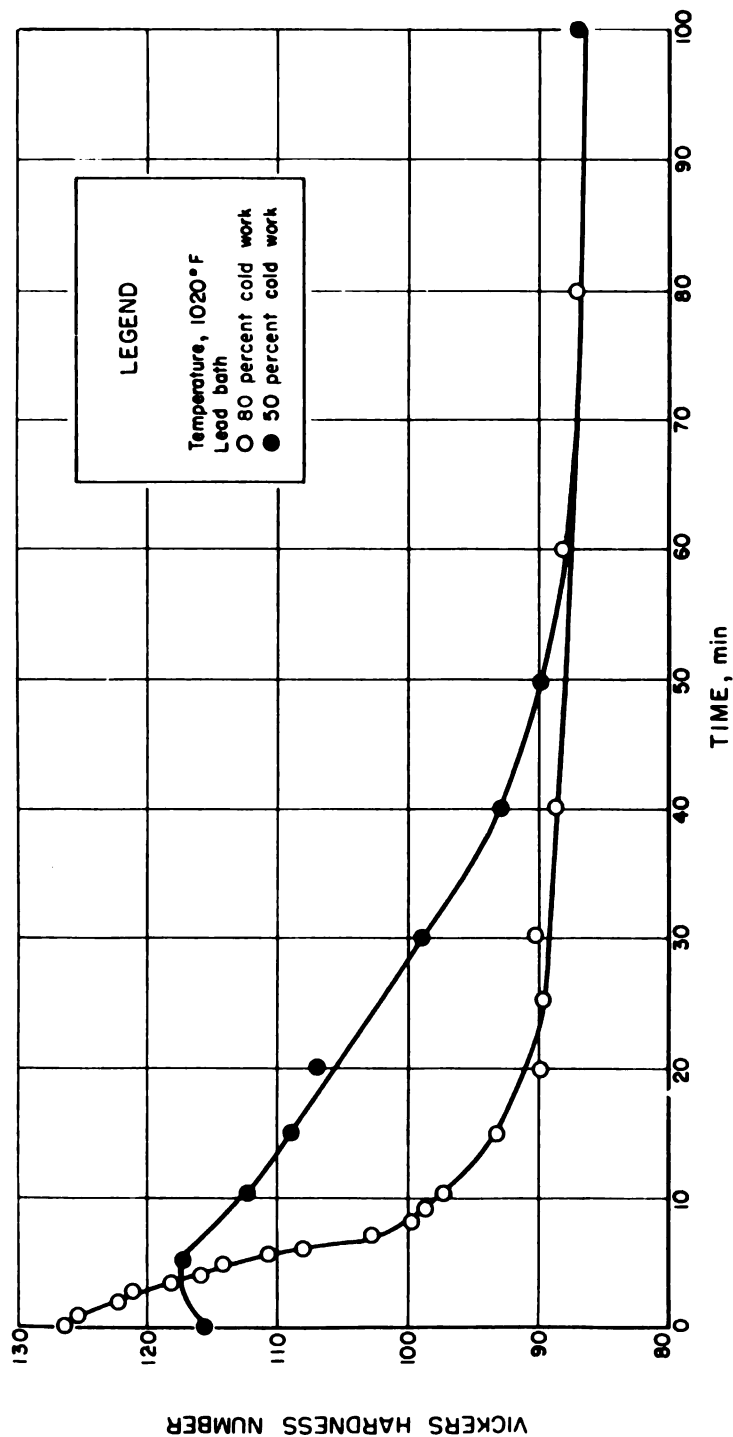


Fig. 1.19.15 — The Effect of Cold Work on the Recrystallization of Bomb-reduced Thorium. Reprinted from "Thorium Alloy Development; Sect. III of Metallurgy Division Quarterly Progress Report for Period Ending October 31, 1950," E. C. Miller and W. H. Bridges, editors, ORNL-910, Feb. 8, 1951.

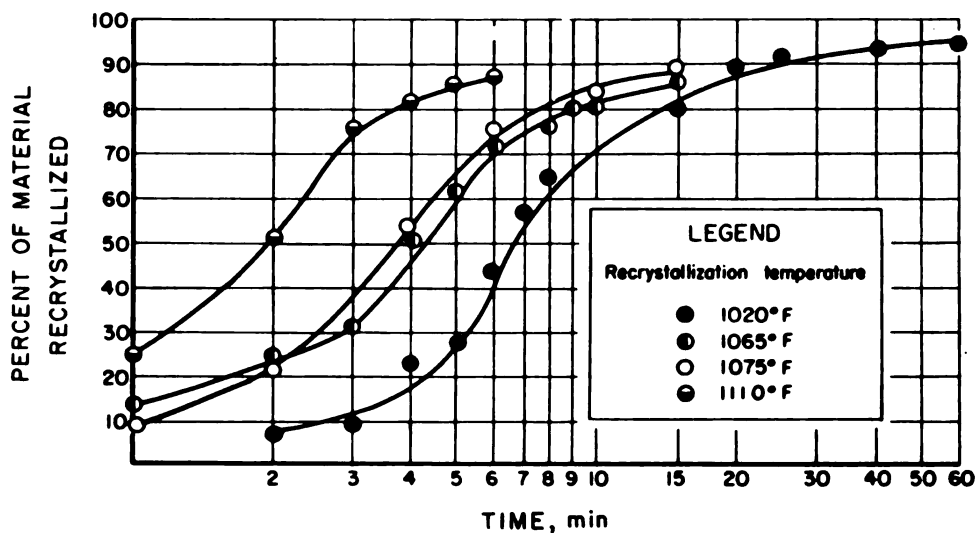


Fig. 1.19.16—Isothermal-recrystallization Curves of Bomb-reduced Thorium. Reprinted from "Interim Report on Metallurgy of Thorium and Thorium Alloys," D. E. Hamby, ORNL-1090, Dec. 7, 1951.

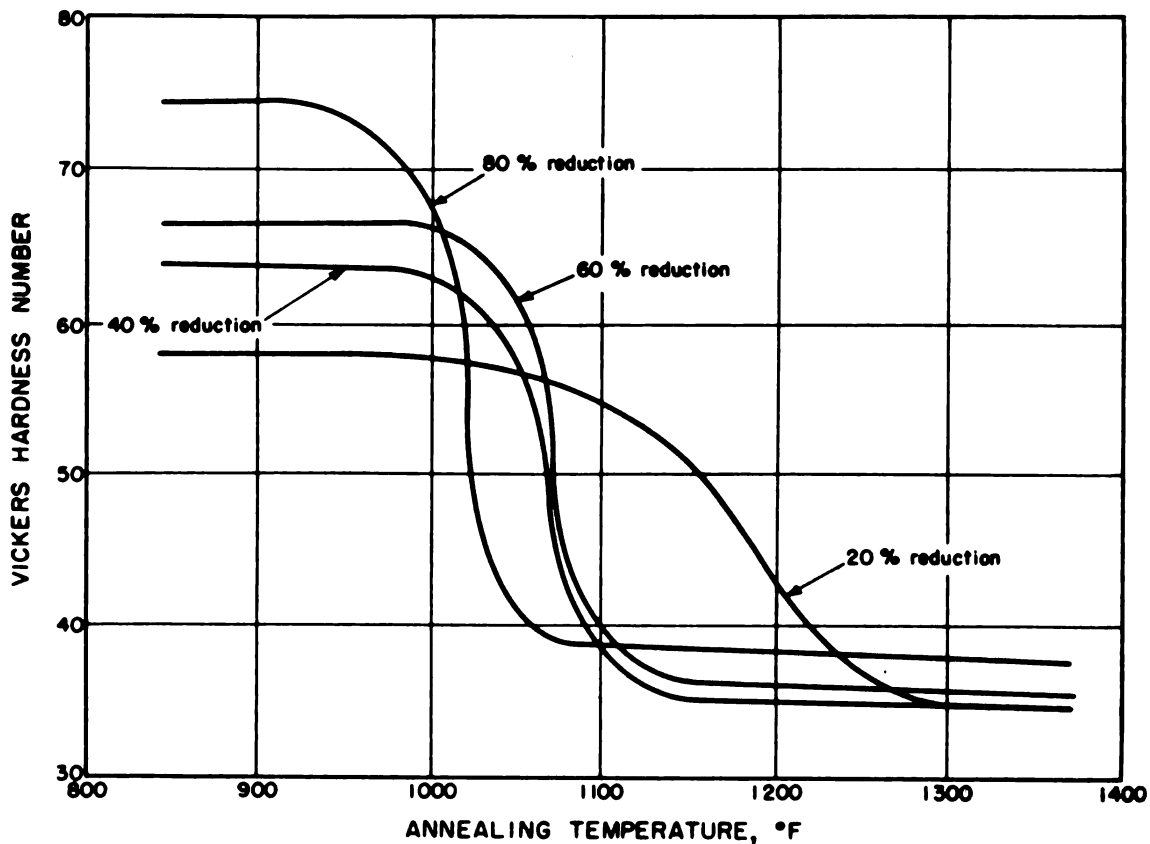


Fig. 1.19.17—The Effect of Cold Work on the Recrystallization of Iodide Thorium Heated 1 hr at Temperature. Constructed from Data of E. J. Boyle, ORNL, Sept. 1, 1952.

CORROSION BEHAVIOR

CORROSION IN AIR

Thorium has been shown to oxidize in air according to the parabolic law at low temperatures and linearly at higher temperatures. Scaling tests in air, nitrogen, argon, and carbon dioxide indicate that in air a marked increase in the rate of scaling occurs between 1470° and 1650°F. There is also a marked increase in the rate of scaling after 1 hr at 1470°F. The weight gain after $\frac{1}{2}$ hr at 1470°F in various gases is shown below:

Atmosphere	Weight Gain, gm/cm ²
Air	6.0
Tank nitrogen	4.4
Purified nitrogen	2.0
Tank argon	1.0
Purified argon	0.75

Figure 1.19.18 indicates the weight gain of bomb-reduced thorium heated in air at temperatures between 570° and 930°F. A thorium: 2-percent-beryllium alloy shows somewhat higher weight gains under similar conditions.

CORROSION IN WATER

Thorium becomes covered with oxide and gains weight when exposed to boiling, distilled water. Weight gains of 0.03 mg/(cm²)(hr) to losses of 0.006 mg/(cm²)(hr) have been reported. An anodic pretreatment is reported to reduce the rate of attack in water.

Coupling aluminum and thorium in water has no effect on the thorium, but the corrosion rate of the aluminum is increased. Thorium alloys containing 1 to 4 percent silicon are similar to pure thorium, as are alloys containing 2.75 to 5.53 percent iron. The addition of 0.4, 2, and 4 percent beryllium adversely affects the corrosion characteristics. Alloys with 2 and 4 percent of niobium and 0.3 to 1.24 percent carbon are also less resistant than pure thorium.

Other data indicate that there is no significant difference in the corrosion rates of thorium and thorium alloys containing 2 to 6 weight-percent of niobium, chromium, titanium, or zirconium in distilled water at 200°F. The chromium alloys are a possible exception, but the improvement in corrosion rates is small and probably not significant.

The addition of thorium nitrate (0.3 M) or nitric acid (0.5 M and 15.4 M) causes partial disintegration of pure thorium samples.

In water at 300°F, thorium is severely attacked and partially disintegrated after an exposure of 144 hr. At 600°F in water, the attack is extremely rapid, and the safety diaphragm on the bomb was ruptured after only a 2-hr exposure.

CORROSION IN LIQUID METALS

The corrosion resistance of thorium in eutectic sodium-potassium alloy is excellent. At 1110°F, the corrosion rate during a static 6-day test in NaK which had been cleaned with uranium chips was 0.006 mg/(cm²)(hr). The corrosion rate increased as the oxygen content of the NaK increased. The effect of stress on the corrosion resistance was negligible.

Thorium is not significantly attacked by lithium in 6 days at 1110°F but is completely disintegrated by gallium at 1110°F. Severe attack occurs in pure bismuth in 1 hr at 1650°F, but only slight oxidation is observed on samples immersed for 1 hr in pure lead at 1650°F. A sample immersed in lead at 1830°F for 40 hr dissolved.

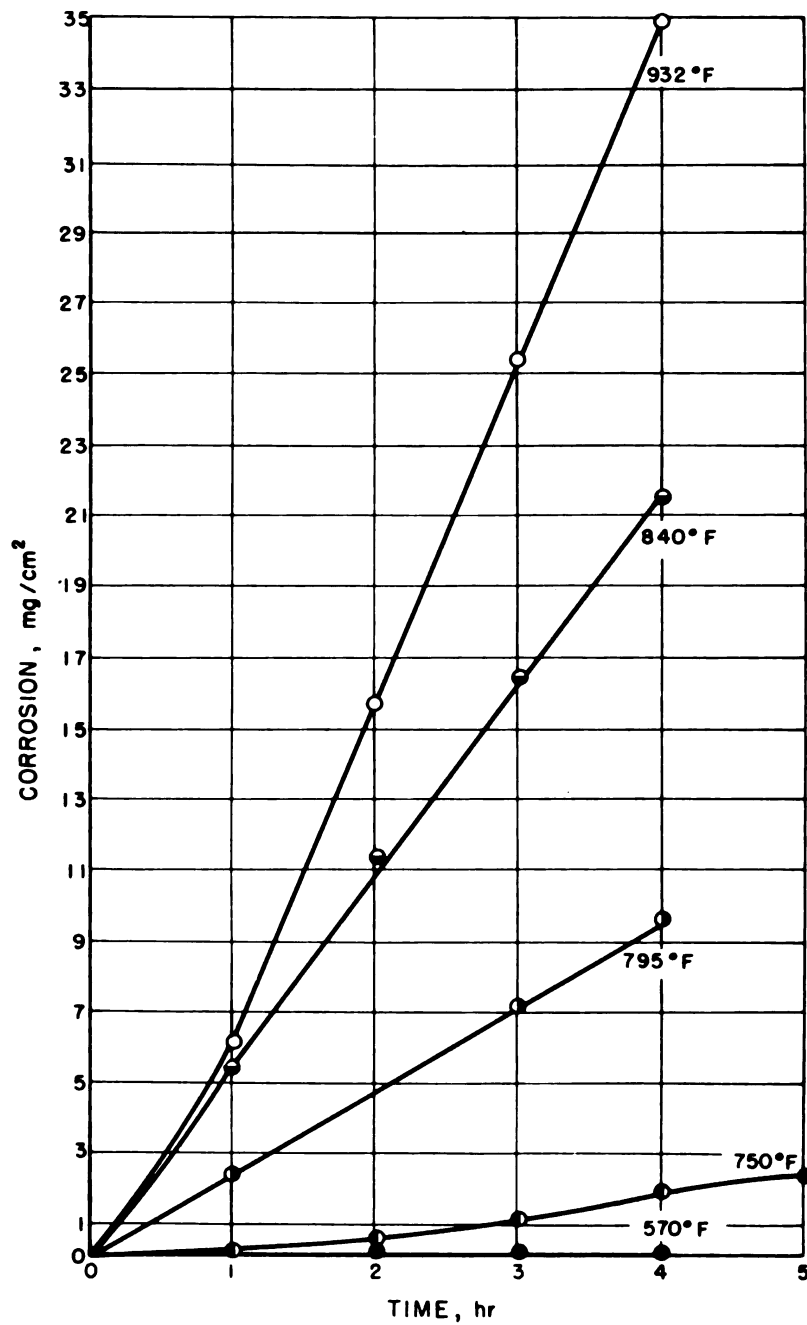


Fig. 1.19.18— Corrosion of Thorium in Air at Various Temperatures. Submitted by Battelle Memorial Institute, July 1, 1952.

PROTECTIVE TECHNIQUES

ELECTROPLATING

Electroplating techniques have been developed for plating aluminum, zinc, chromium, iron, nickel, copper, tin, lead, silver, indium, gold, and rhodium on thorium. A chemical pretreatment is necessary in order to obtain good adherence and uniform deposition. This treatment consists of a 3- to 5-min anodic pickle of the abraded or vapor-blasted surface in 10 volume-percent HCl with a current density of 125 to 250 amp/sq ft at room temperature. This is followed by a 3- to 10-min chemical pickle in 10-percent sulfuric acid at room temperature. The sample is then rinsed in tap water and immersed in the desired plating bath. With the above pretreatment, good adherence was obtained with each of the metals previously indicated.

Electrolytic metal removal or "electromachining" can be used to remove surface layers up to 0.040 in. thick. The bath consists of 25 volume-percent concentrated sulfuric acid, 25 volume-percent phosphoric acid (85 percent), and balance water, and is operated at 150 to 300 amp/sq ft at a temperature of 120° to 130°F. At a current density of 150 amp/sq ft, 0.001 in. of metal is removed in 10 min.

METALLOGRAPHY

Although considerable effort has been devoted to the development of suitable metallographic techniques for thorium, the existing etchants are not entirely satisfactory. It is possible to outline structure; however, this is accomplished at the expense of the inclusions which are present in the metal.

An etch-polish technique for the metallographic preparation of thorium for inclusion study has proven satisfactory. The metal is wet ground by normal procedures through the 600-grit paper, and the polish is accomplished on a lap of Forstmann's cloth with Linde-A abrasive wet with the following solution:

100 cm ³	HNO ₃
100 cm ³	H ₂ O
16 drops	H ₂ SiF ₆

Five to ten turns on an 1150 rev/min wheel treated in this manner are usually enough to prepare the surface for examination.

Electrolytic etchants have produced the best results for grain studies. These etches are applied to a prior-polished surface. Typical etchants are given in Table 1.19.8.

THORIUM ALLOYS

Constitutional diagrams of thorium and aluminum, beryllium, bismuth, carbon, copper, chromium, gold, nickel, silver, sodium, uranium, and zirconium are given in Figs. 1.19.19 through 1.19.30. Pertinent data on the various binary alloy systems are presented in Table 1.19.9.

With the exception of carbon and indium, small additions of up to 5 atomic percent of most elements are ineffective in strengthening bomb-reduced thorium. Figure 1.19.31 shows the relative strengthening effect of the various elements in dilute arc-melted thorium alloys. The effect of these additions on the hardness at room temperature and at 570°F is shown in Fig. 1.19.32. Small additions of titanium, zirconium, and niobium decrease the as-cast hardness of bomb-reduced thorium markedly, probably through a scavenging action on the carbon and oxygen present in the bomb-reduced material. The fabricating characteristics of these alloys have been discussed previously.

The work-hardening characteristics of several dilute binary alloys are illustrated in Fig. 1.19.33. None of the dilute alloys have marked age-hardening characteristics.

The effect of uranium on the tensile properties of bomb-reduced thorium is shown in Fig. 1.19.34. Small additions of uranium increase the strength considerably, and the strength of the alloys increases with increasing uranium content up to 50 percent uranium. The fabricating characteristics of these alloys are good, and the increase in strength with cold work is greater than that of unalloyed bomb-reduced metal.

Table 1.19.8—Electrolytic Etchants for Thorium*

Etchant composition, cm ³	Open-circuit cell voltage, v	Remarks
180 Phosphoric acid 40 Nitric	15	Less than 5 sec etching time required
20 Perchloric acid 200 Water	40	Bath must be cooled
1 Perchloric acid 15 Ethyl alcohol	35	Operate bath at 20°C

*These etchants outline grain structure; however, certain inclusions are severely attacked in the process

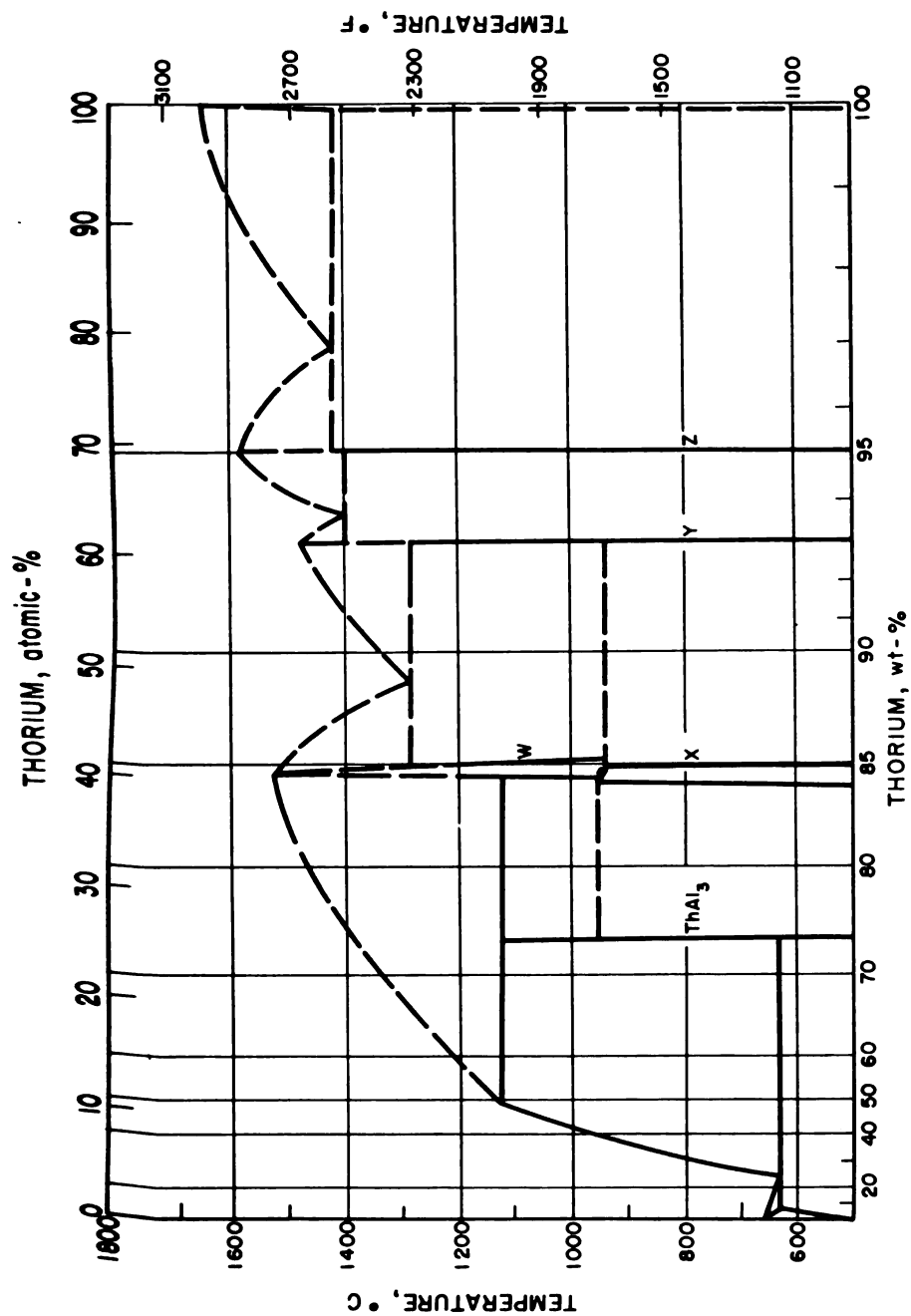


Fig. 1.19.19—The Constitutional Diagram of the System Aluminum-Thorium.
Submitted by Battelle Memorial Institute, July 1, 1952.

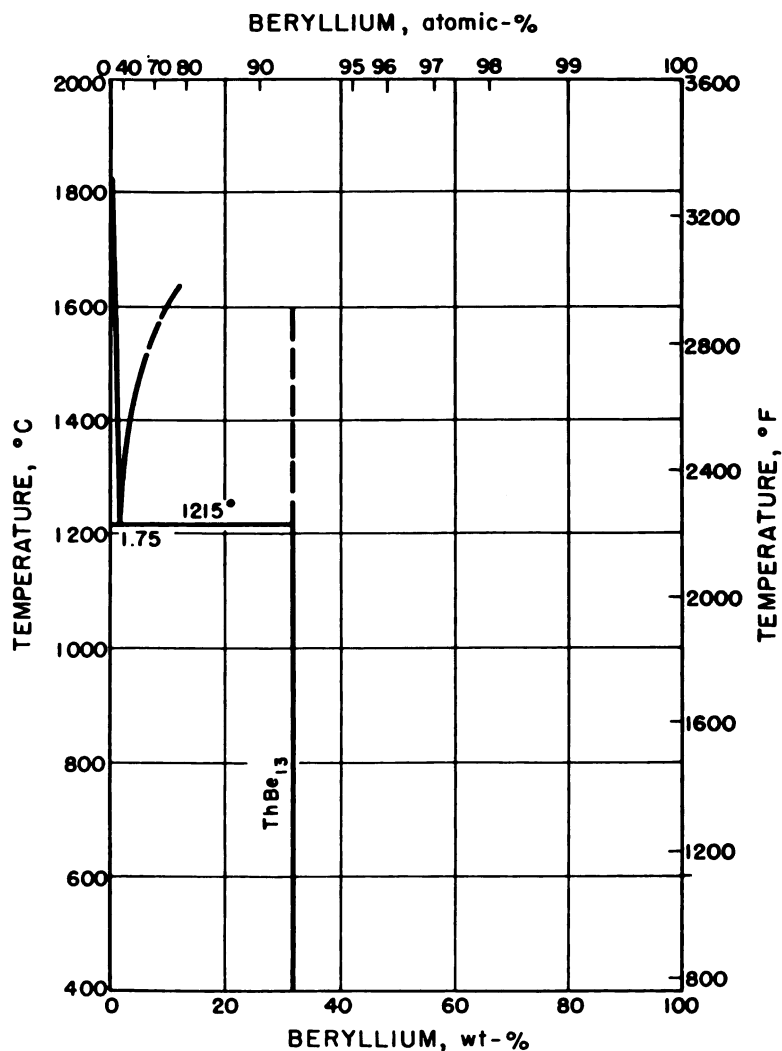


Fig. 1.19.20—The Constitutional Diagram of the System Thorium-Beryllium. Constructed from Data in "Thorium Metallurgy," H. A. Wilhelm, et al., CT-3714, Feb. 22, 1946; "Technological Research—Metallurgy Report for Period Oct. 10 to Nov. 10, 1944," CT-1985, Jan. 4, 1945; and "Progress Report for Feb. 24 to Mar. 3, 1945," F. Foote, et al., CT-2755, Mar. 3, 1945.

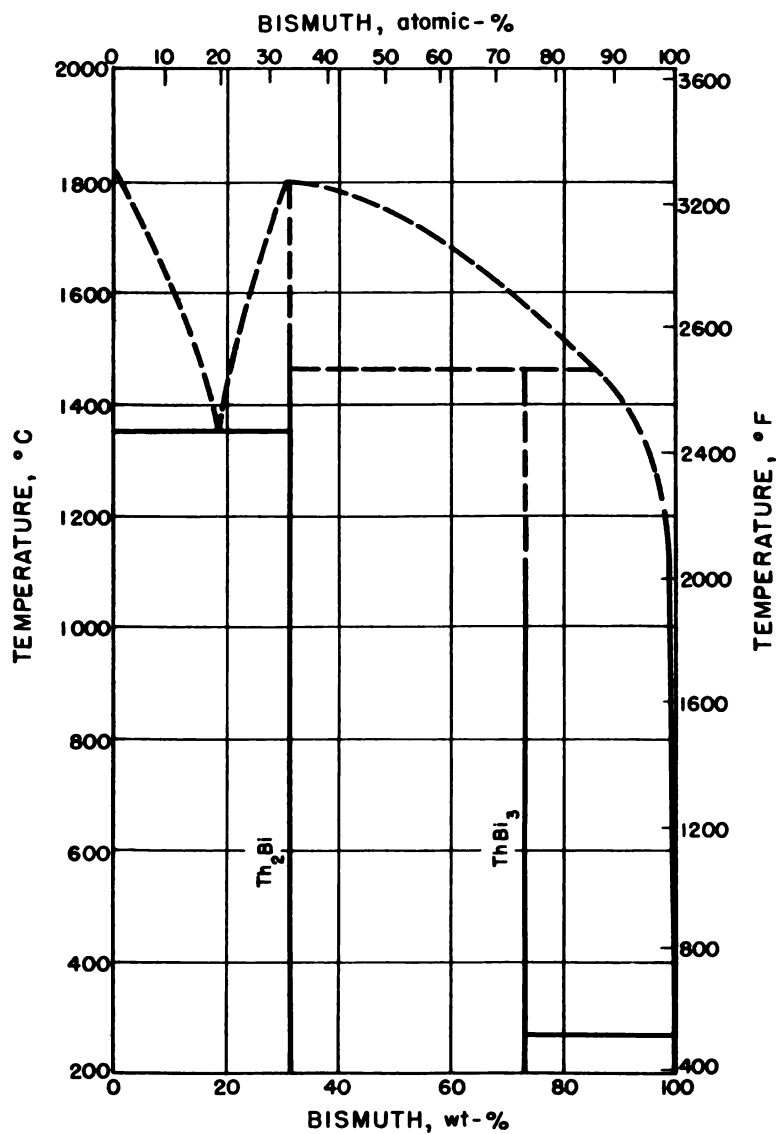


Fig. 1.19.21—The Constitutional Diagram of the System Thorium-Bismuth. Reprinted from "Thorium Alloys: The Thorium-Bismuth System," H. B. Johnson, ISC-48, July 12, 1950.

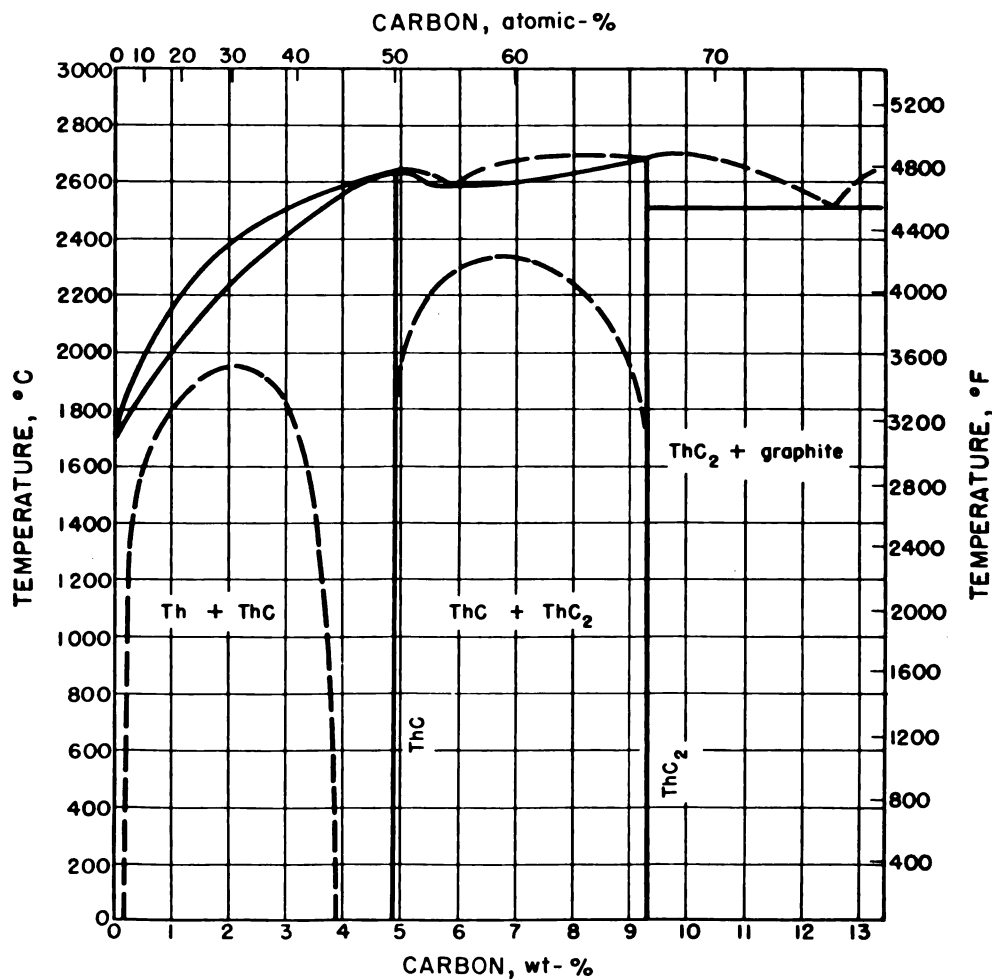


Fig. 1.19.22—The Constitutional Diagram of the System Thorium-Carbon. Reprinted from "Thorium-Carbon System," P. Chiotti, AECD-3072, June 5, 1950.

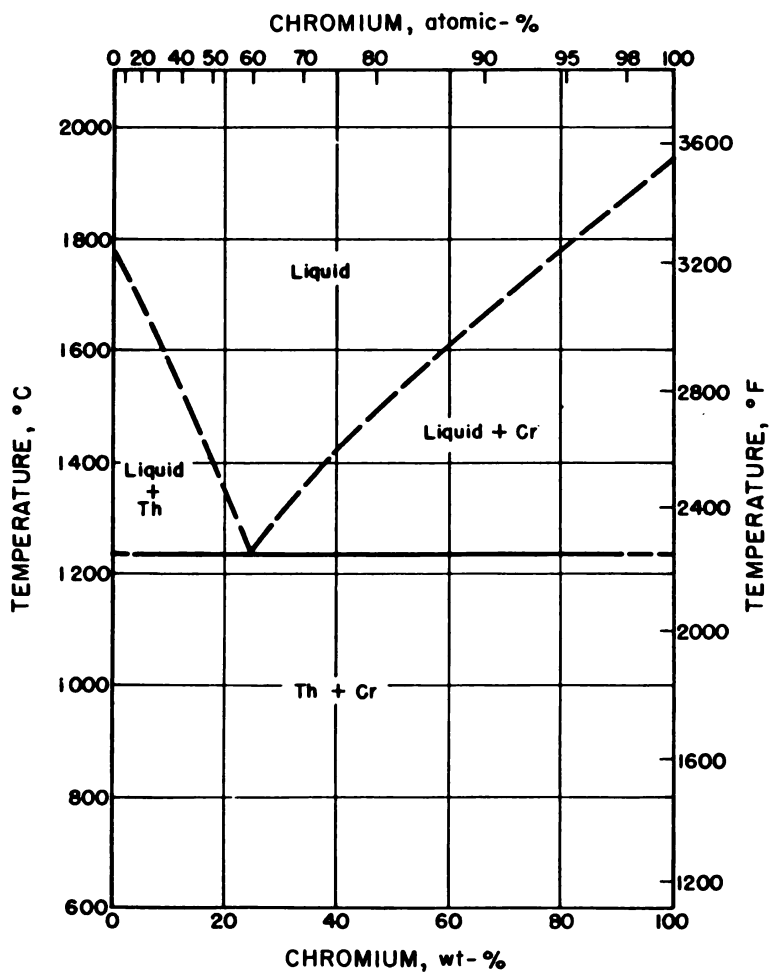


Fig. 1.19.23—The Constitutional Diagram of the System Thorium-Chromium. Reprinted from "Thorium Metallurgy," H. A. Wilhelm, et al., CT-3714, Feb. 22, 1946.

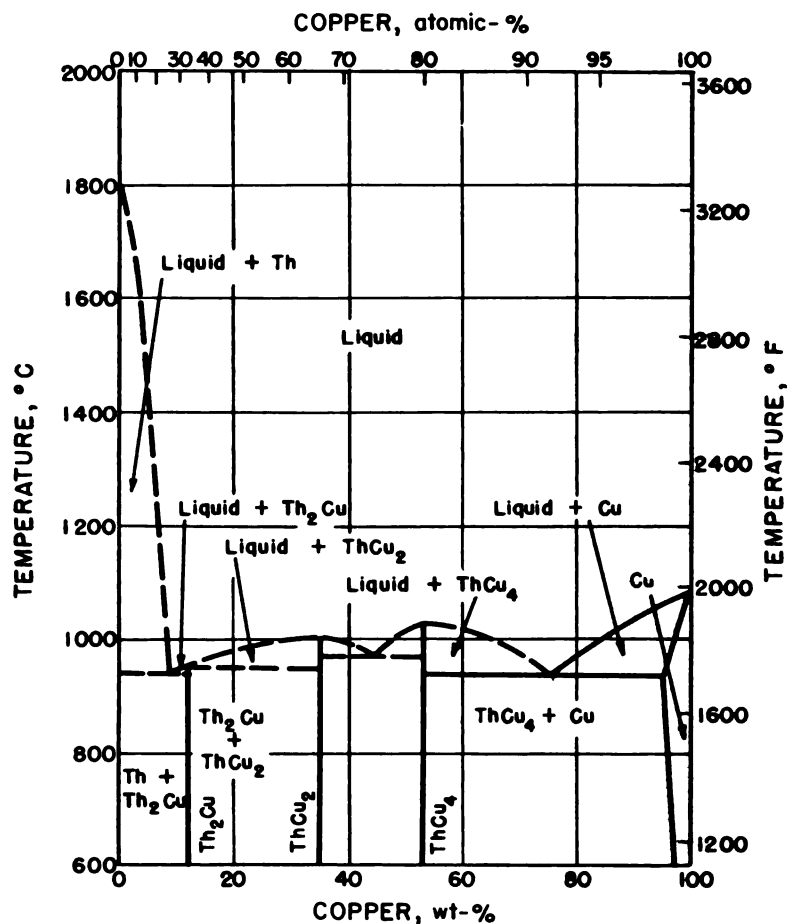


Fig. 1.19.24—The Constitutional Diagram of the System Thorium-Copper. Constructed from Data of "Thorium Metallurgy," CT-3714, Feb. 22, 1946; G. Grube and L. Botzenhardt, Z. Elektrochem., Vol 48, p 418, 1942; and "Report of the Metallurgical Conference Held at Mass. Inst. Technol., Feb. 20-21, 1947," H. G. Rickover, et al., M-3430, Mar. 10, 1947.

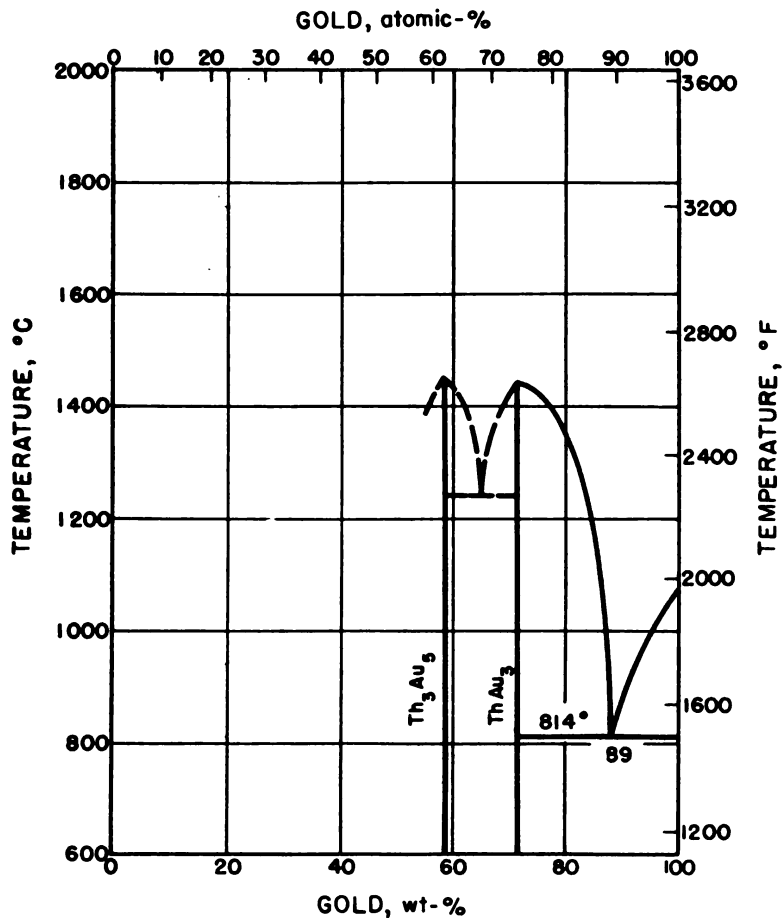


Fig. 1.19.25—The Constitutional Diagram of the System Thorium-Gold. Reprinted from E. Raub and M. Engel, Z. Elektrochem., Vol 49, p 487, 1943.

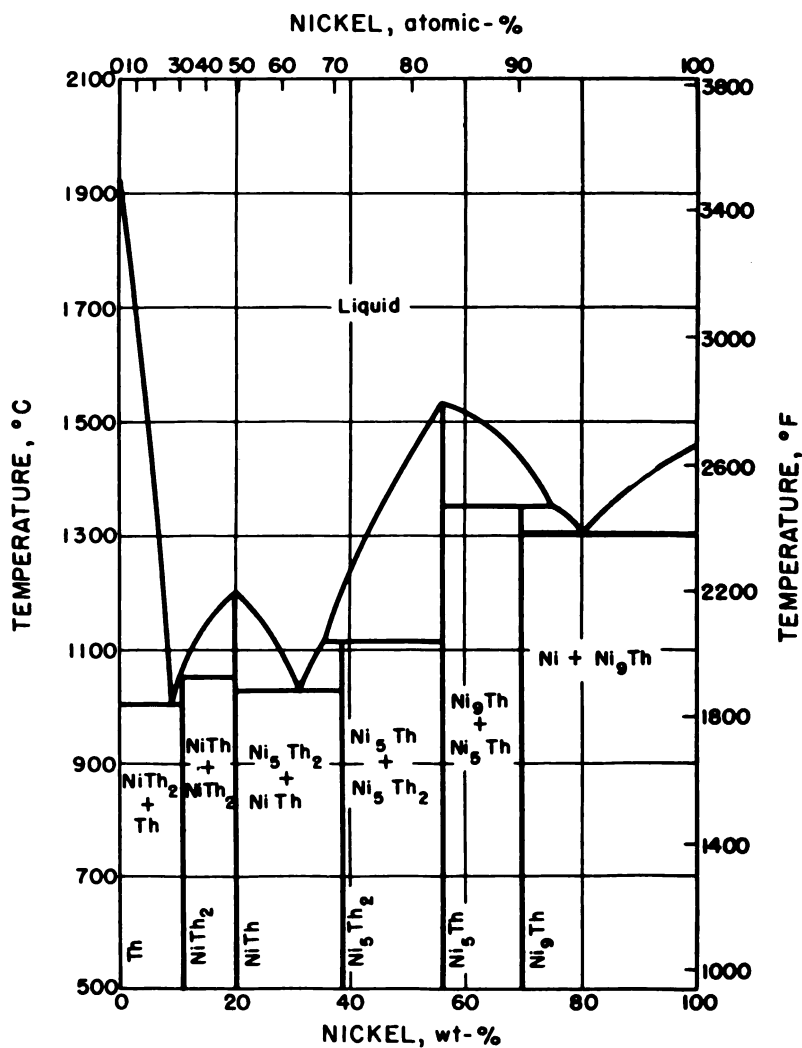


Fig. 1.19.26—The Constitutional Diagram of the System Thorium-Nickel. Reprinted from Horn and Basserman, *Z. Metallkunde*, Vol 39, p 273, 1948.

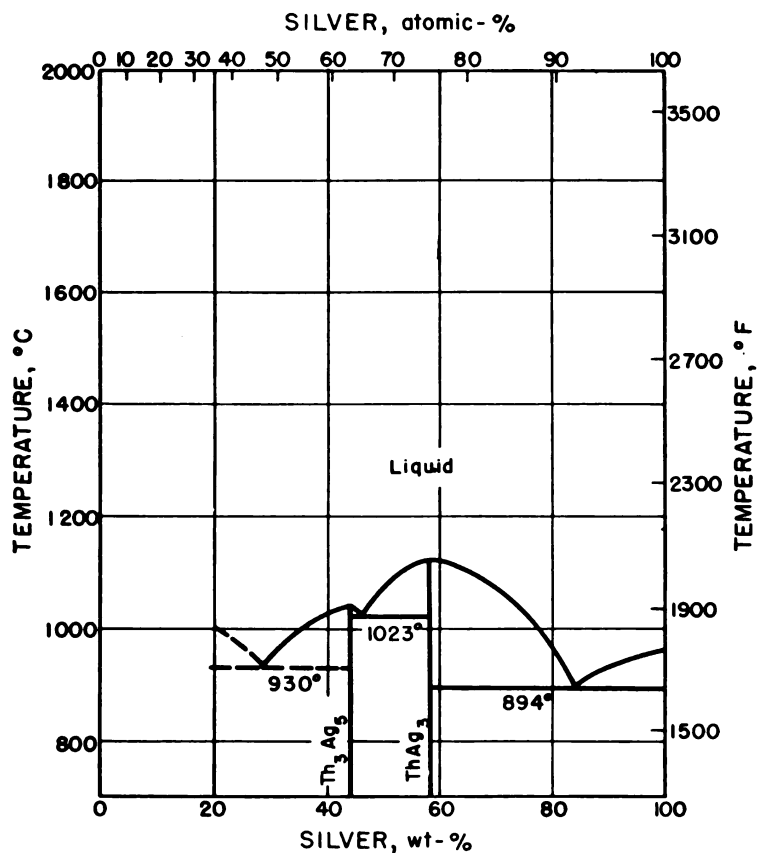


Fig. 1.19.27—The Constitutional Diagram of the System Thorium-Silver.
Reprinted from E. Raub, *Z. Metallkunde*, Vol 40, p 431, 1949.

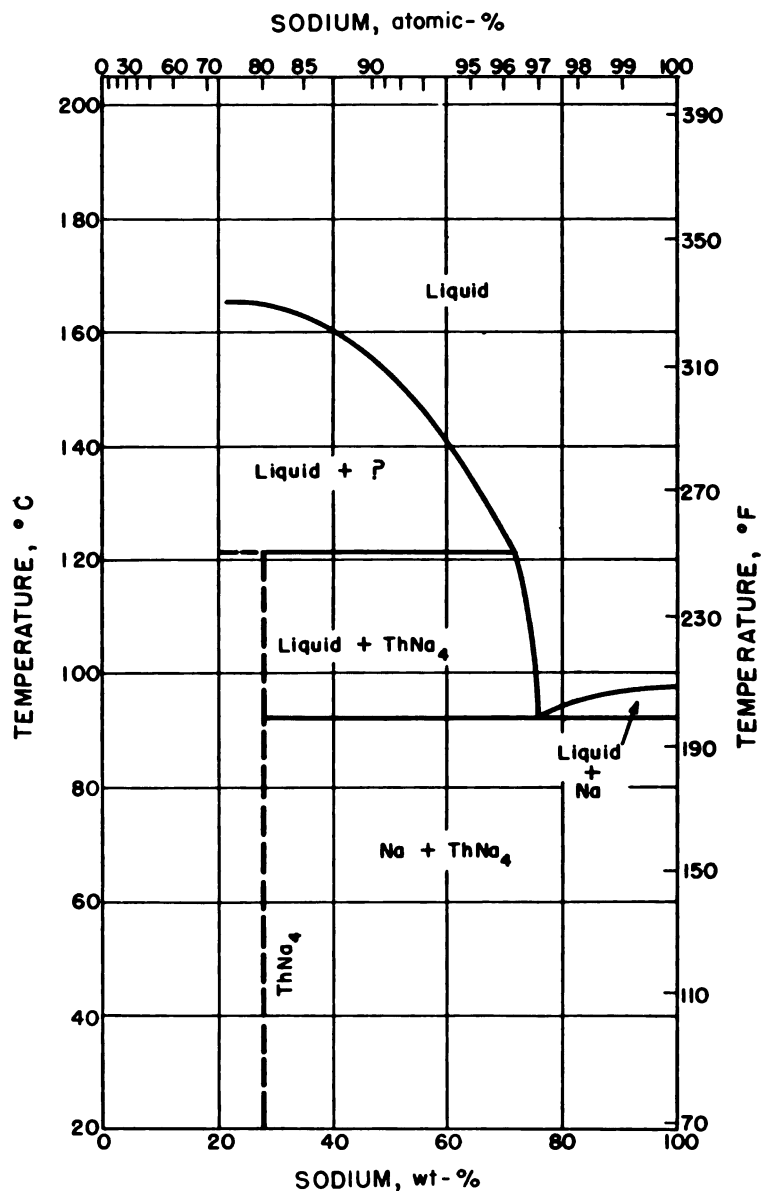


Fig. 1.19.28—The Constitutional Diagram of the System Thorium-Sodium. Reprinted from G. Grube and L. Bozenhardt, *Z. Elektrochem.*, Vol 48, p 418, 1942.

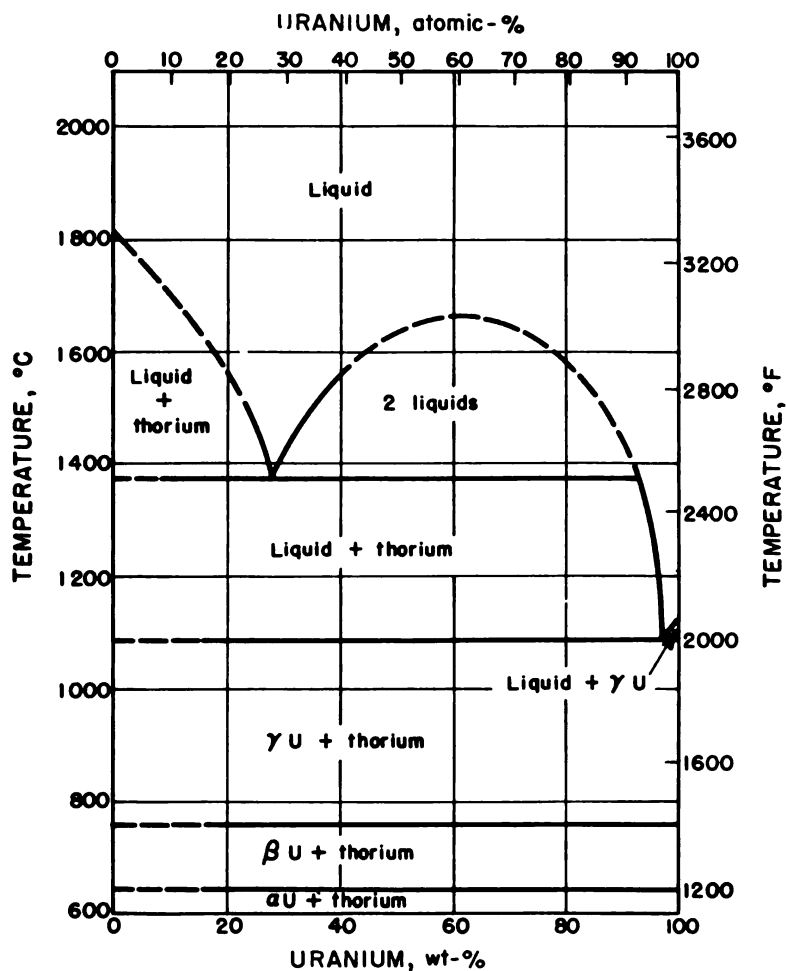


Fig. 1.19.29—The Constitutional Diagram of the System Thorium-Uranium. Reprinted from "Some Studies on the Uranium-Thorium-Zirconium Ternary Alloy System," O. N. Carlson, ISC-102, June 5, 1950.

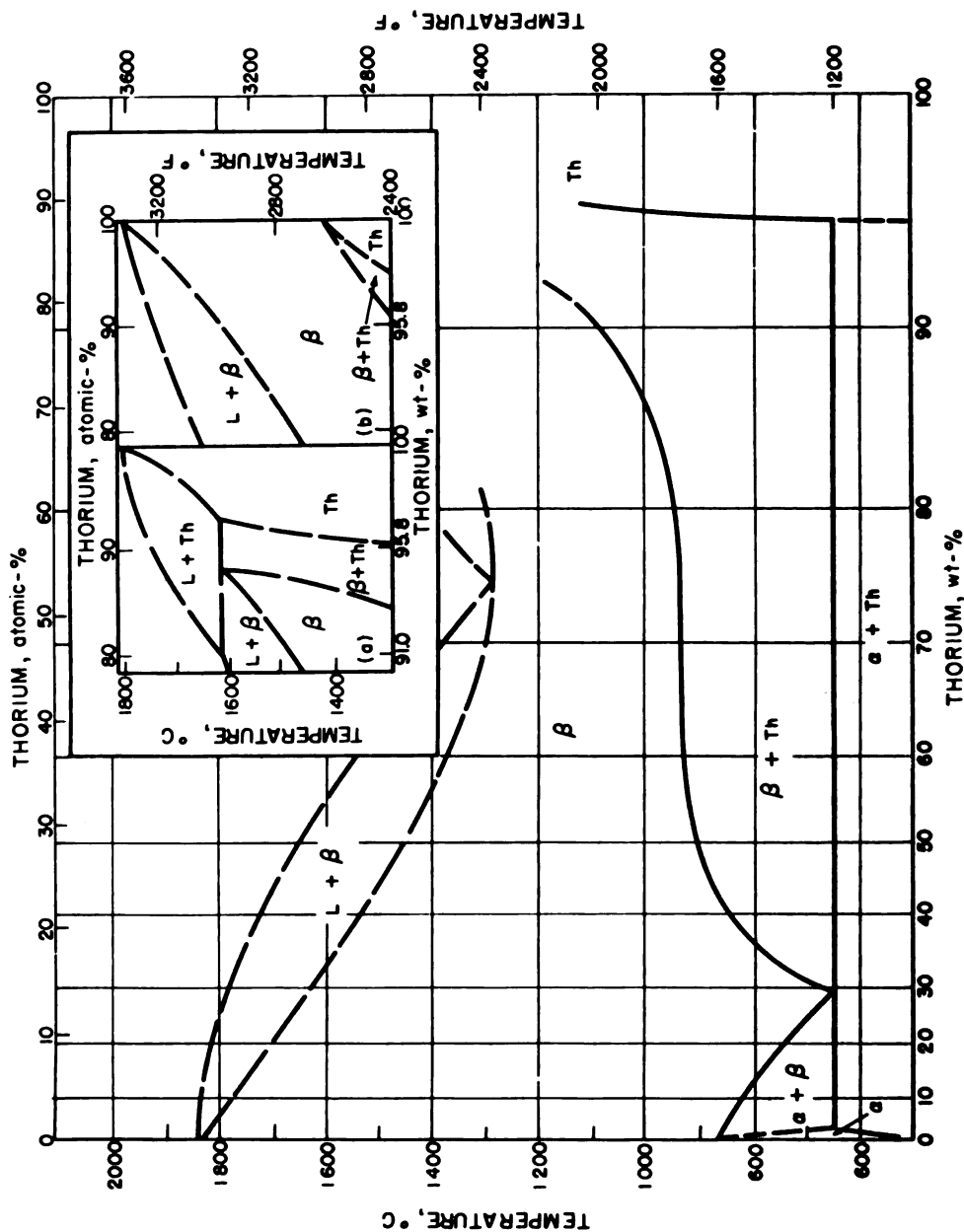


Fig. 1.19.30—The Constitutional Diagram of the System Zirconium-Thorium. Submitted by Battelle Memorial Institute, July 1, 1952. Inserts (a) and (b) show proposed thorium-rich end of the diagram; (a) is based on the existence of an allotropic modification of thorium, and (b) is based on no allotropy.

Table 1.19.9 — Binary Alloys of Thorium

System	Features of diagram	Intermetallic compounds		
		Composition	Structure*	Lattice constants, A
Th-Al	As illustrated	ThAl ₃
		ThAl _x
Th-Be	As illustrated	ThBe ₁₃	F.c.c.	a ₀ = 10.395
Th-Bi	As illustrated	Th ₂ Bi
		ThBi ₃
Th-B	Th-ThB ₄ eutectic at ~1550°C	ThB ₄	Tetragonal	a ₀ = 7.256, c ₀ = 4.113
		ThB ₃	Cubic	...
Th-C	As illustrated	ThC	F.c.c.	a ₀ = 5.29
		ThC ₂	Monoclinic	a ₀ = 6.53
				b ₀ = 4.24
				c ₀ = 6.56
				B = 104°
Th-Ce	Complete solid solubility
Th-Cr	As illustrated
Th-Co	...	Th ₇ Co ₃	Hexagonal	a ₀ = 9.81, c ₀ = 6.16
		ThCo ₄	...	a ₀ = 5.01, c ₀ = 3.97
Th-Co	...	ThCo ₅
		ThCo	Complex	...
		ThCo ₂
		ThCo ₃
		Th ₂ Cu	B.c.t.	a ₀ = 7.28, c ₀ = 5.74
Th-Cu	As illustrated	ThCu ₂ †	Hexagonal	a ₀ = 4.35, c ₀ = 3.74
		ThCu ₄
		Th ₃ Au ₅
Th-Au	As illustrated	ThAu ₅
		ThH ₂	B.c.t.	a ₀ = 4.09, c ₀ = 5.02
Th-H	...	ThH _x (ThH _{3.75} ThH ₄)	Cubic	...
		Th ₇ Fe ₃	Hexagonal	a ₀ = 9.83, c ₀ = 6.14
Th-Fe	Complex-eutectic at 46 atomic-percent Fe and 860°C	ThFe	Complex	...
		ThFe ₉ -ThFe ₁₉	Complex	...
Th-La	No data			
Th-Pb	No data			
Th-Mn	Eutectic at 911°C and >20 atomic-percent Mn	ThMn ₂	Hexagonal	a ₀ = 5.47, c ₀ = 8.93
		Th ₂₄ Mn ₉₂	F.c.c.	a ₀ = 12.50
		ThMn ₁₂	Couples	...
Th-Hg	...	ThHg ₃	H.c.p.	a ₀ = 3.38, c ₀ = 4.72
Th-Mo	No data	ThHg ₄		
Th-Ni	As illustrated	ThNi ₃
		ThNi ₅
		Th ₂ Ni ₅
		ThNi
		Th ₂ Ni
Th-Nb	Eutectic at the Th rich side; mp ~1315°C
Th-N	...	Th ₃ N ₄	F.c.c.	a ₀ = 5.18
		ThN	NaCl type	...
Th-O	...	ThO ₂	Fluorite type	...
Th-Si	Eutectic at about 13 weight-percent Si; mp >1300°C	ThSi ₂	B.c.t.	...
Th-Ag	...	ThAg ₃
		Th ₃ Ag ₅ †
Th-Na	As illustrated	ThNa ₄ (?)
Th-P	No data	ThP	NaCl type	...
		Th ₃ P ₄	D ₃ ^h	...

Table 1.19.9—(Continued)

System	Features of diagram	Intermetallic compounds		
		Composition	Structure*	Lattice constants, A
Th-S	...	ThS ₂
		Th ₇ S ₁₂
		Th ₂ S ₃
		ThS
Th-Ta	No compounds; solid solubility of Ta in Th is low
Th-Tl	No data			
Th-Sn	No data			
Th-Ti	Eutectic at about 12 weight-percent Ti and at ~1175°C
Th-W	No compounds			
Th-U	As illustrated
Th-V	No data			
Th-Zn	6-7 weight-percent Zn lowers mp to ~1200°C	Th ₂ Zn	B.c.t.	a ₀ = 7.60, c ₀ = 5.64
Th-Zr	As illustrated

*F.c.c. = face-centered cubic; b.c.t. = body-centered tetragonal; h.c.p. = hexagonal close packed

†Pyrophoric

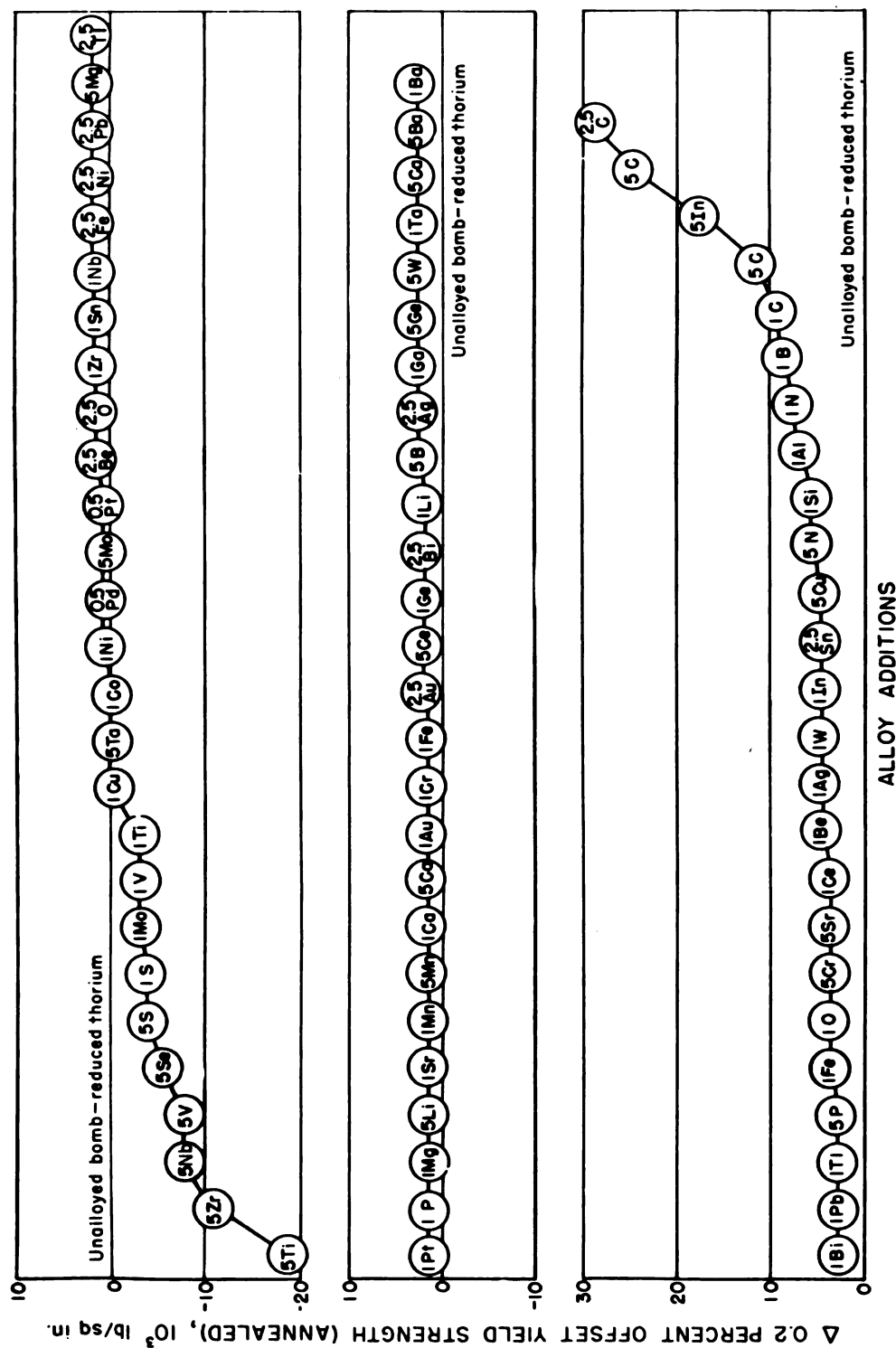


Fig. 1.19.31—The Effect of Alloying Additions Up to 5 Atomic-percent on the Yield Strength of Arc-melted Binary Thorium Alloys. Reprinted from "A Study of Thorium-base Alloys," R. M. Goldhoff, H. R. Ogden, R. I. Jaffee, BMI-720, Dec. 26, 1951.

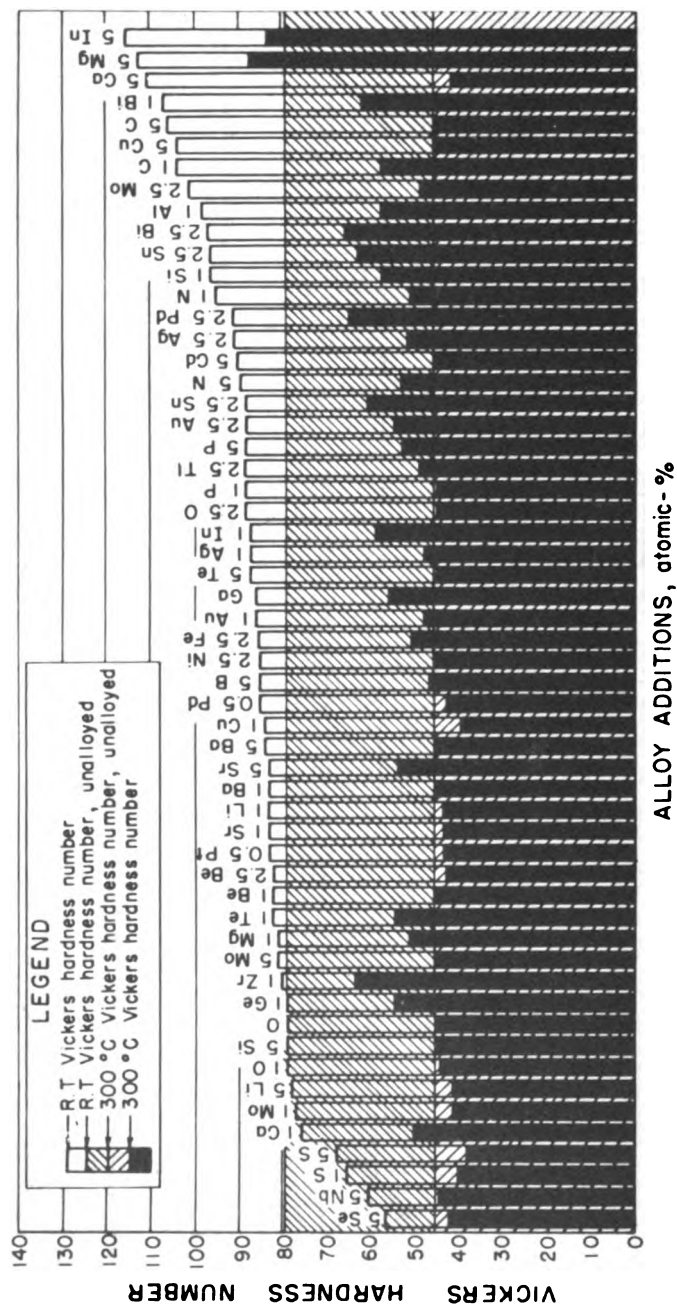


Fig. 1.19.32—Comparison of Room-temperature Hardness and Hardness at 570°F for Fabricated Binary Thorium Alloys Annealed 2 hr at 1560°F. Reprinted from "A Study of Thorium-base Alloys," R. M. Goldhoff, H. R. Ogden, R. I. Jaffee, BMI-720, Dec. 26, 1951.

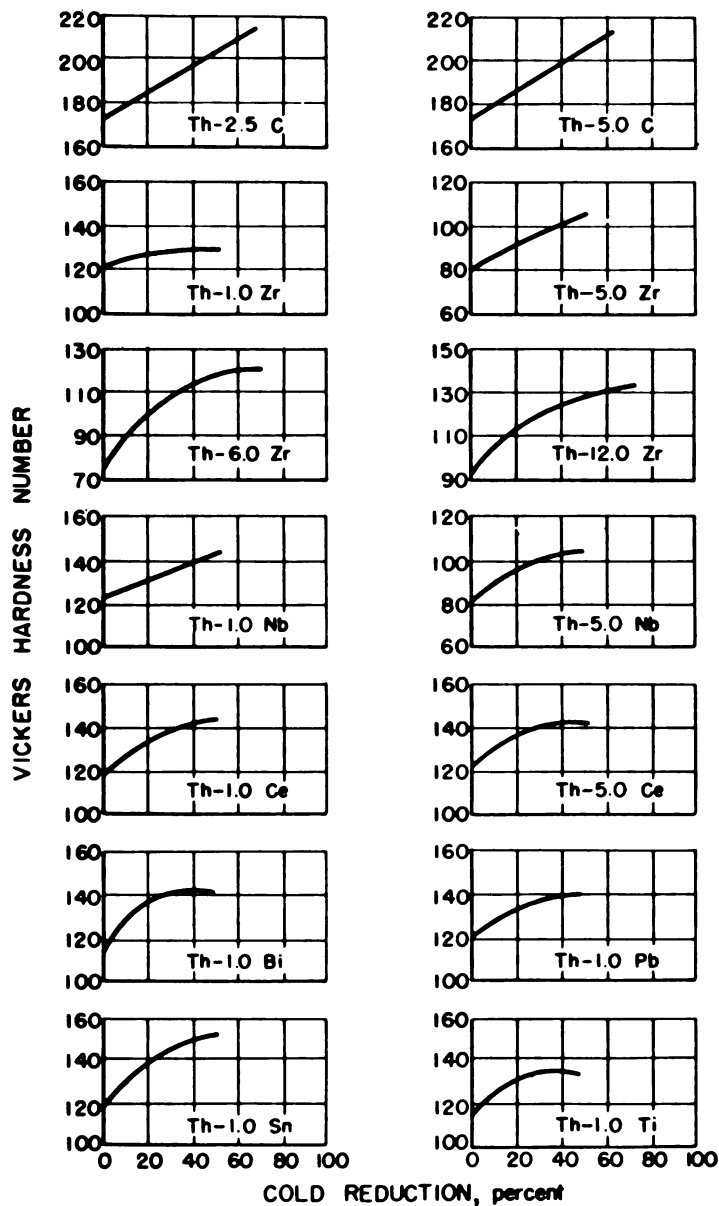


Fig. 1.19.33—Curves of Hardness Versus Percent Cold Reduction for Several Binary Thorium Alloys. Submitted by Battelle Memorial Institute, July 1, 1952.

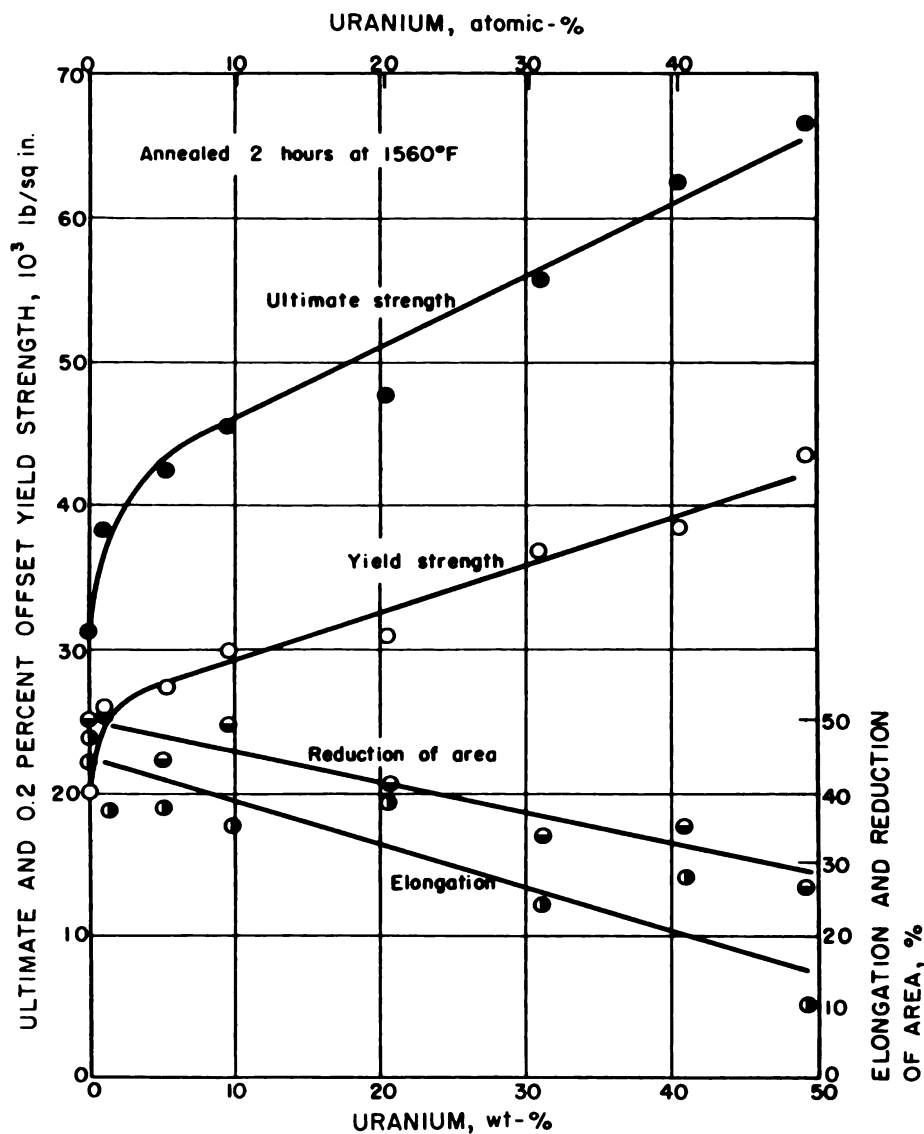


Fig. 1.19.34 — The Effect of Uranium on the Room-temperature Tensile Properties of Bomb-reduced Thorium. Submitted by Battelle Memorial Institute, July 1, 1952.

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- Iowa State College, G. C. Danielson, et al., ISC-200, Jan. 18, 1952 (classified).
- Oak Ridge National Laboratory, D. E. Hamby, ORNL-1090, Dec. 7, 1951 (classified).
- Battelle Memorial Institute, M. C. Udy and F. W. Boulger, BMI-89, Sept. 15, 1951 (classified).
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CHAPTER 1.20

Titanium and Its Alloys

H. R. Ogden

INTRODUCTION

Titanium has often been called the "sister metal" of zirconium and with good cause. Both elements have similar crystal structures, undergo crystal changes at elevated temperatures, and are equally difficult to refine. The histories of the two metals are parallel, and it has only been in the last decade that the processes for refining these metals have been advanced to the stage where production can be listed in tons rather than pounds. Titanium, however, does not have the low thermal-neutron-absorption cross section that makes zirconium so attractive for reactor use. Instead, its mechanical properties, low density, and amenability to alloying have made it attractive as a structural material, and hence, the commercialization of titanium and its alloys has proceeded rapidly. Tables 1.20.1 and 1.20.2 list the nominal compositions of titanium and commercial titanium alloys.

REACTOR APPLICATION

Titanium, a relatively new metal with much promise as a structural material because of its high strength/weight ratio and its good corrosion resistance, has as yet no specific application in reactors. In the current development of thermal reactors, titanium has been by-passed in favor of metals having more desirable thermal-neutron-absorption properties, but this restriction on its use should be lifted when structural materials for intermediate or fast reactors are considered.

ABUNDANCE AND AVAILABILITY

Titanium is the ninth most abundant element in the earth's crust. In a list of useful metals, it is outranked only by aluminum, iron, and magnesium and is much more plentiful than lead, copper, zinc, tin, and the balance of the more common metals. Its affinity for oxygen, however, makes it difficult to refine, and consequently, the technology of titanium has advanced only in recent years to the stage where relatively pure metal is available on a commercial scale. In view of the abundant supply of raw material, which occurs not only as a minor constituent in most of the earth's crust but also in highly concentrated form in readily available locations, the promise of a large, continuous supply of titanium is assured. The titanium minerals ilmenite ($\text{FeO} \cdot \text{TiO}_2$) and rutile (TiO_2) are the most important from a commercialization viewpoint.

Table 1.20.1—Typical Analyses of Titanium

Type of Titanium	Composition, %											
	C	O	N	Al	Cu	Fe	Mg	Mn	Mo	Ni	Si	Sn
Iodide titanium	0.01 - 0.03	0.005 - 0.01	0.001 - 0.004	0.013 - 0.05	0.0015 - 0.002	0.0035 - 0.025	0.0015 - 0.002	0.005 - 0.013	0.0015	0.003	<0.03	0.001 - 0.01
Magnesium-reduced titanium sponge	.01 - .03	.05 - .15	.01 - .05	<.005	<.03	.03 - .2	.04 - .12	.03 - .06	<.01	<.03
Commercial-purity, arc-melted titanium (low hardness)	.02	.05 - .1	.01 - .0503 - .2
Commercial-purity, arc-melted titanium (high-hardness)	.02	.1 - .25	.01 - .1503 - .2
Graphite-melted titanium	.25 - .8	.05 - .15	.01 - .1503 - .2

Table 1.20.2—Nominal Composition of Commercial Titanium Alloys

Designation	Producer*	Nominal composition, %									
		C	O	N	Al	Fe	Cr	Mn	Other		
MST 2Al-2Fe	MST	0.5	2	2		
MST 3Al-5Cr	MST	.5	3	5		
MST 2.5Fe-2.5V	MST	.5	2.5	2.5V		
RC-130A	RC	.2 max	7	...		
RC-130B	RC	.2 max4	4	...		
Ti-140A	TMC	.08 max	0.2	0.1	...	2.1	2	...	1.9 Mo		
Ti-150A	TMC	.02	.25	.02	...	1.3	2.7		
Ti-150B	TMC	.02	Trace	.02	...	5	5	...	5 Mo		
Ti-175A	TMC	.02	.5	.04	...	3.0	1.5		

*MST = Mallory-Sharon Titanium Corporation; RC = Rem-Cru Titanium, Incorporated; TMC = Titanium Metals Corporation of America

In the past, before a method of refining titanium was developed, titanium ores were mined extensively for their TiO_2 content which was used in the pigments industry. In this country, ilmenite-rutile sands occurring in Florida and Virginia were the main sources of TiO_2 ; ilmenite was also imported from India and Norway. In 1946, the largest known titanium-ore reserve was discovered in the Allard Lake district of eastern Quebec. Two large high-grade ore bodies consisting of a mixture of ilmenite and hematite have been reported and are estimated to contain many hundreds of millions of tons of ore.

In the United States, many localities contain extensive titanium mineral deposits which are sufficiently concentrated to be classed as ore bodies. Some of these have been mined, but for the most part, they can be considered as untouched ore reserves. Deposits of titanium-bearing ores exist in New York, North Carolina, Minnesota, Rhode Island, Wyoming, Montana, California, Colorado, Oklahoma, and New Mexico.

The Titanium-Zirconium Panel, Metallurgical Advisory Board, gives the following estimates of production from 1950 through 1952:

	Tons/yr
2nd half of 1950	150
1st half of 1951	400
2nd half of 1951	700
1st half of 1952	1000
2nd half of 1952	5000

EXTRACTION AND PURIFICATION

Because of the affinity of titanium for oxygen, nitrogen, and carbon, special techniques must be employed to win the metal from its ores. Not only does titanium react readily with these three elements, but it dissolves all three in large quantities when in the liquid state and retains large quantities of oxygen and nitrogen in solid solution. Except for a small solid solubility, however, carbon is precipitated as TiC on solidification of titanium. Titanium is reactive enough at elevated temperatures to attack all known oxide refractories.

The discovery of the Kroll process for producing titanium metal has caused the rapid development of titanium metallurgy. In this process, titanium metal is obtained by reducing TiCl_4 which can be produced readily from the ore, with molten magnesium in an iron vessel containing an inert atmosphere. This method is of necessity a batch process, but it can probably be developed, with modifications, to a large-scale commercial process. This development is currently in progress.

Discussion of extractive processes is limited here to ilmenite, the most prevalent ore. A simplified flowsheet showing the necessary steps is shown in Fig. 1.20.1. Ilmenite ore can be treated by smelting, acid treatment, or direct chlorination. When ilmenite occurs with an iron ore such as hematite, the smelting process is preferable because of the iron recovery. The titanium, which goes into the slag, is recovered as TiO_2 in a subsequent acid treatment. The acid treatment is the same as that used to purify the high-titanium ilmenite ores. The direct chlorination process eliminates the smelting or acid-treating steps, but because the titanium tetrachloride produced directly from the ore contains impurities, it must be further refined before it can be used in the magnesium-reduction process.

The magnesium-reduction process produces titanium of variable purity, depending upon the operating conditions. The major impurities are oxygen and nitrogen from the atmosphere and iron from the reaction vessel. Some batches of titanium have been produced which contain very small amounts of these elements, but the usual quality of titanium contains about 0.05-0.25 percent oxygen, 0.01-0.02 percent nitrogen, and 0.05-0.25 percent

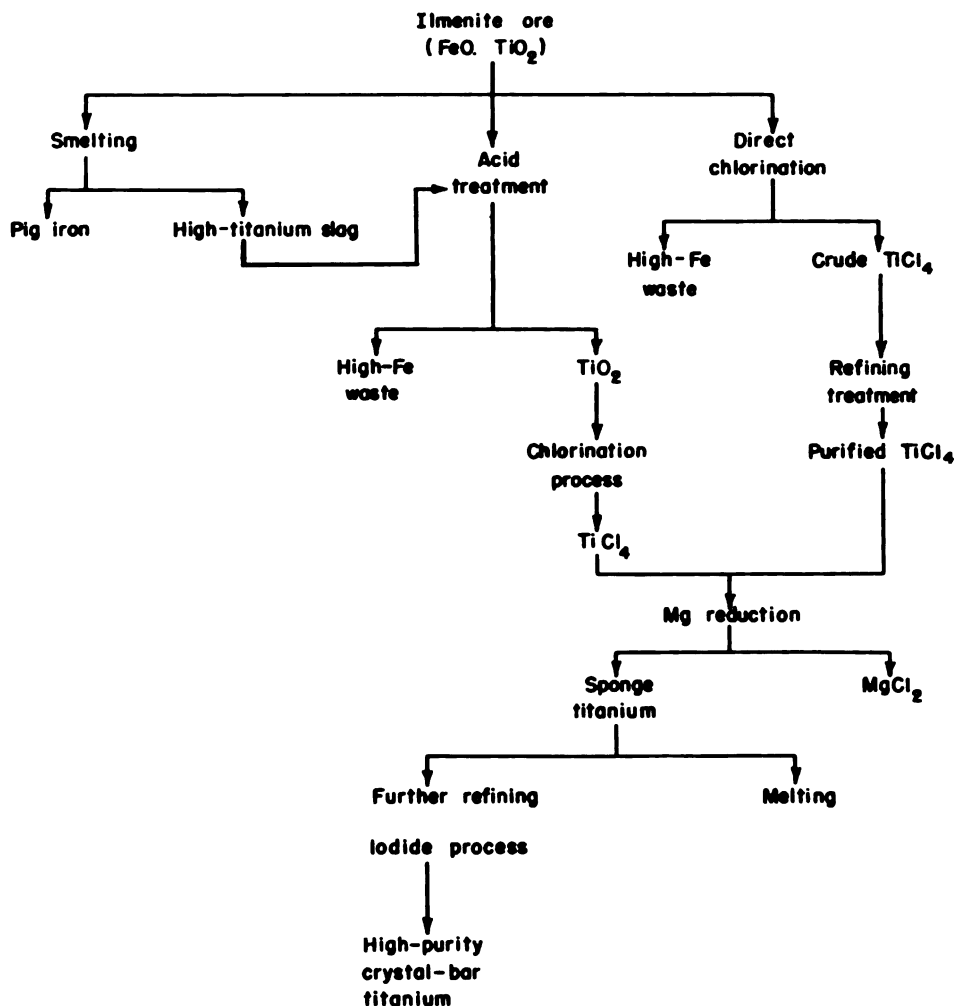


Fig. 1.20.1—Simplified Flowsheet for the Extraction and Purification of Titanium. Prepared by Battelle Memorial Institute.

iron. Since the hardness of titanium is directly proportional to its oxygen and nitrogen content, titanium produced by this method is classed as “high-” or “low-hardness” titanium.

Magnesium-reduced titanium can be further refined by the iodide-dissociation process. This process has been used for many years to produce the purest titanium available for research purposes. It consists of heating a vessel (from which all air has been excluded) containing impure titanium metal and a small amount of iodine to 300° to 400°F where the iodine reacts with the crude titanium to form volatile titanium tetraiodide. A hot filament within the vessel causes the tetraiodide to dissociate whereupon titanium is deposited on the filament. The free iodine then reacts with more crude titanium to complete the cycle. Titanium produced by this method is relatively free of oxygen and nitrogen, although some metallic impurities are carried over in various amounts. Typical analyses of iodide and sponge titanium are shown in Table 1.20.1.

PHYSICAL AND CHEMICAL CONSTANTS

The **physical** and chemical constants of titanium are listed in Table 1.20.3, and selected physical constants of some titanium alloys are given in Table 1.20.4. Titanium is a silvery gray metal having a density intermediate between those of aluminum and steel. It has a high melting point, but because it absorbs oxygen and nitrogen at temperatures above 900°F, it is not suitable for high-temperature use in air. Both its electrical conductivity and

Table 1.20.3—Physical and Chemical Constants of Titanium

Thermal-neutron-absorption cross section,* barns/atom	5.6 ± 0.4
Density,† gm/cm ³	4.507
Melting point, °C	1690
Boiling point, °C	3535
Heat of sublimation (25°C), cal	106,500
Specific heat (0° to 500°C),‡ cal/(gm)(°C)	0.1386
Entropy (25°C), cal/(mole)(°C)	7.24
Coefficient of linear thermal expansion (25°C), per °C	8.5 × 10 ⁻⁶
Thermal conductivity (25°C),§ cal/(sec)(cm)(°C)	0.41
Electrical resistivity (20°C), μohm-cm	47.8
Allotropic transformation temperature, °C	882
Lattice constants, Å	
Alpha, hexagonal close-packed, 25°C	a ₀ = 2.9504
	c ₀ = 4.6833
Beta, 900°C	a ₀ = 3.3065

*The reader is referred to Volume 1, "Reactor Physics," for a detailed discussion of cross-section versus neutron energy

†Gm/cm³ × 62.43 = lb/cu ft

‡Cal/(gm)(°C) × 1 = Btu/(lb)(°F)

§Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

Table 1.20.4—Some Physical Constants of Titanium Alloys

Alloy*	Density,† gm/cm ³	Melting range, °C	Thermal conductivity,‡ cal/(sec)(cm)(°C)	Coefficient of linear thermal expansion, per °C	Specific heat,§ cal/(gm)(°C)	Electrical resistivity, μohm-cm
MST 2Al-2Fe	4.55	9.7 × 10 ⁻⁶	...	118
MST 3Al-5Cr	4.58	9.0 × 10 ⁻⁶	...	140
MST 2.5Fe-2.5V	4.61	9.2 × 10 ⁻⁶	...	78
RC-130A	4.69	1400 - 1500
RC-130B	4.69	1600 - 1700
Ti-140A	4.66	18.0 × 10 ⁻⁶	...	78.7
Ti-150A	4.64	...	0.034 - 0.041	9.0 × 10 ⁻⁶	0.129	60
Ti-150B	4.64034 - .041	9.0 × 10 ⁻⁶	.129	...
Ti-175A	4.64034 - .041	9.0 × 10 ⁻⁶	.129	60

*See Table 1.20.1 for compositions

†Gm/cm³ × 62.43 = lb/cu ft

‡Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

§Cal/(gm)(°C) × 1.0 = Btu/(lb)(°F)

thermal conductivity are very low, about the same as those of an 18-8 stainless steel. Consequently, the use of titanium is impractical in applications that require good heat transfer or electrical conductivity. The low thermal expansion of titanium, however, may be of value in applications involving cyclical temperature fluctuations.

MECHANICAL PROPERTIES

GENERAL

Pure titanium is a relatively weak, ductile metal having a modulus of elasticity of about 15,000,000 lb/sq in. In this pure state, it is doubtful that titanium will have much use as a structural material. However, commercial-grade titanium, which contains small amounts of the interstitial elements, oxygen and nitrogen, as well as a small amount of iron, is much stronger and can be regarded as a useful structural material. Since the strength of commercial titanium depends on the amounts of the dissolved interstitial elements present, a range of properties is generally obtained. Figure 1.20.2 shows the effect of carbon, oxygen, and nitrogen on the mechanical properties of high-purity titanium. The basic mechanical properties of high-purity titanium and of commercial-purity titanium of two grades are given in Table 1.20.5.

The commercial alloys available today are of the alpha-beta and metastable-beta types. (See subsequent discussion of alloys.) These alloys have high strengths and are suitable for most structural purposes. Certain alloys have been designed for sheet applications and others for bar-stock applications. The governing factors involved in choosing the alloy for the application are composition, structure, and formability. The nominal mechanical and physical properties of these alloys are given in Table 1.20.6.

EFFECT OF COLD WORK

The properties of high-purity or commercial-grade titanium, even though it undergoes an allotropic transformation, can not be appreciably changed by heat-treatment. Other than alloying, therefore, improvements in properties are possible only through the use of cold work or by warm working below the recrystallization temperature. The data given in Table 1.20.7 illustrate the effect of cold working on the properties of sheet titanium and provide a comparison between the properties of forged bar stock and annealed sheet. Although titanium loses strength rather rapidly at elevated temperatures, the effectiveness of cold work is maintained at temperatures up to at least 800°F because of the low recovery rate in this temperature range. This is illustrated by Fig. 1.20.3. Figure 1.20.4 shows time-temperature curves for removing work hardening from cold-worked titanium; the time required to completely remove work hardening from cold-worked titanium is in excess of 5000 hr at temperatures below 800°F.

CREEP AND ELEVATED TEMPERATURE PROPERTIES

The creep strength of annealed titanium at room temperature is rather low when compared with the yield strength. However, cold working improves the room-temperature creep resistance of titanium. Between 400° and 600°F, both annealed and cold-worked titanium show negligible creep at stresses up to the yield strength; however, the yield strength is quite low at these elevated temperatures. Typical room-temperature creep curves given in Fig. 1.20.5 show that the creep strength of titanium at room temperature may be taken as 60 percent of the yield strength. Typical stress-rupture curves for commercial-purity titanium are given in Fig. 1.20.6.

Stress-to-rupture data for commercial-purity titanium in calcium-gettered (oxygen-free) sodium at 800° and 1000°F are given in Table 1.20.8.

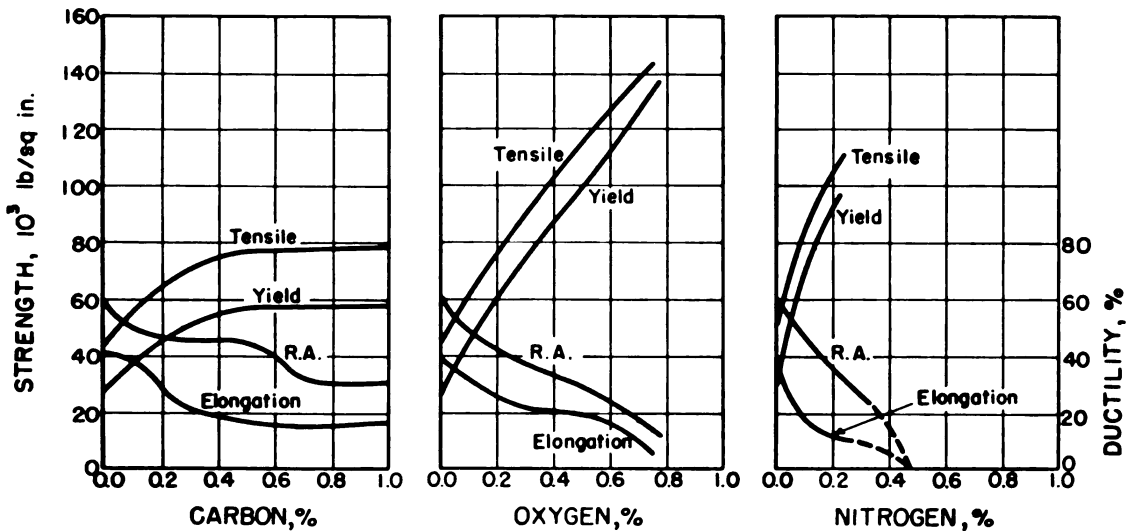


Fig. 1.20.2—The Effect of Carbon, Oxygen, and Nitrogen on the Mechanical Properties of High-purity Titanium. Reprinted from R. I. Jaffee, H. R. Ogden, and D. J. Maykuth, *Alloys of Titanium With Carbon, Oxygen and Nitrogen*, Trans. AIME, Vol 188, 1950.

Table 1.20.5—Mechanical Properties of Titanium

Property	High-purity, iodide-refined titanium	Commercial-purity titanium	
		Low-hardness	High-hardness
Hardness, Vickers No.	80–100	160–180	200–220
Tensile strength, 10^3 lb/sq in.	30–40	65–75	85–100
Yield strength, 10^3 lb/sq in.	16–24	45–55	70–85
Elongation, %	40–60	20–30	20–25
Reduction of area, %	70–90	45–70	40–50
Elastic modulus, 10^6 lb/sq in.	15.5	15.5	15.5
Impact strength (room temperature), ft-lb	40–100	30–60	15–25
Shear strength, 10^3 lb/sq in.	82
Modulus of rigidity, 10^6 lb/sq in.	6.6
Modulus of rupture, 10^3 lb/sq in.	79
Work-hardening characteristics			
$\sigma = B\delta^n$			
B, 10^3 lb/sq in.	75–85
n	0.25–0.35

Table 1.20.6—Nominal Mechanical Properties of Commercial Titanium Alloys

Alloy*	Form	Condition	Yield strength (0.2% offset), lb/sq in.	Tensile strength, lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Modulus of elasticity, 10 ⁶ lb/sq in.	Hardness Rockwell	Hardness Brinell
MST 2Al-2Fe	Sheet (0.040 in.)	Annealed 1 hr at 1300°F	...	140,000	14	...	17	R _A 68	...
		Cold worked 37%	...	180,000	6	...		R _A 70	...
	Forgings	Hot forged 80%	135,000	145,000	12	35		R _A 68	...
MST 3Al-5Cr	Forgings	Hot forged 80%, Furnace cooled	153,000	165,000	8	25	17	R _A 71	...
			...	165,000	10	...		R _A 73	...
MST 2.5Fe-2.5V	Sheet (0.040 in.)	Annealed 1 hr at 1300°F	125,000	135,000	10	...		R _A 65	...
		Cold worked 37%	170,000	175,000	2	...	15	R _A 68	...
	Forging	Hot forged 80%	105,000	130,000	12	35		R _A 65	...
RC-130A	Sheet	Annealed	130,000	150,000	25	35	15.6	R _C 33-36	...
RC-130B	Bar	Annealed	140,000	150,000	20	40	
	Forging	As forged	135,000	150,000	15	30	15.5	R _C 33-36	...
Ti-150A	Plate	Annealed	120,000 (min)	152,000	12 (min)	...	16	...	341
	Forgings, hot-rolled bars	Annealed	120,000 (min)	150,000	15 (min)	341
Ti-175A	Plate	Annealed	140,000 (min)	172,000	8 (min)	379
	Forgings, hot-rolled bars	Annealed	140,000 (min)	170,000	10 (min)	...	16	...	379
Ti-150B	Sheet and strip	Annealed	135,000 (min)	160,000	10	...		R _C 35	...
	Plate	Annealed	135,000 (min)	160,000	10	...	16	...	322

*See Table 1.20.2 for compositions

Table 1.20.7—Room-temperature Properties of Commercially Pure Titanium (High Hardness)

Condition	Tensile Properties					Compressive Properties		
	Modulus of elasticity, 10 ⁶ lb/sq in.	Proportional limit, 10 ³ lb/sq in.	Yield strength, 10 ³ lb/sq in.	Ultimate strength, 10 ³ lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Yield strength, 10 ³ lb/sq in.	Ultimate strength, 10 ³ lb/sq in.
Forged bar	15	55	85	90	15	25	75	95
Annealed sheet	15	52	80	90	20	55	70	...
1/4-hard sheet	15	...	105	120	12	35	85	...
Full-hard sheet	15	...	115	130	10	30	100	...

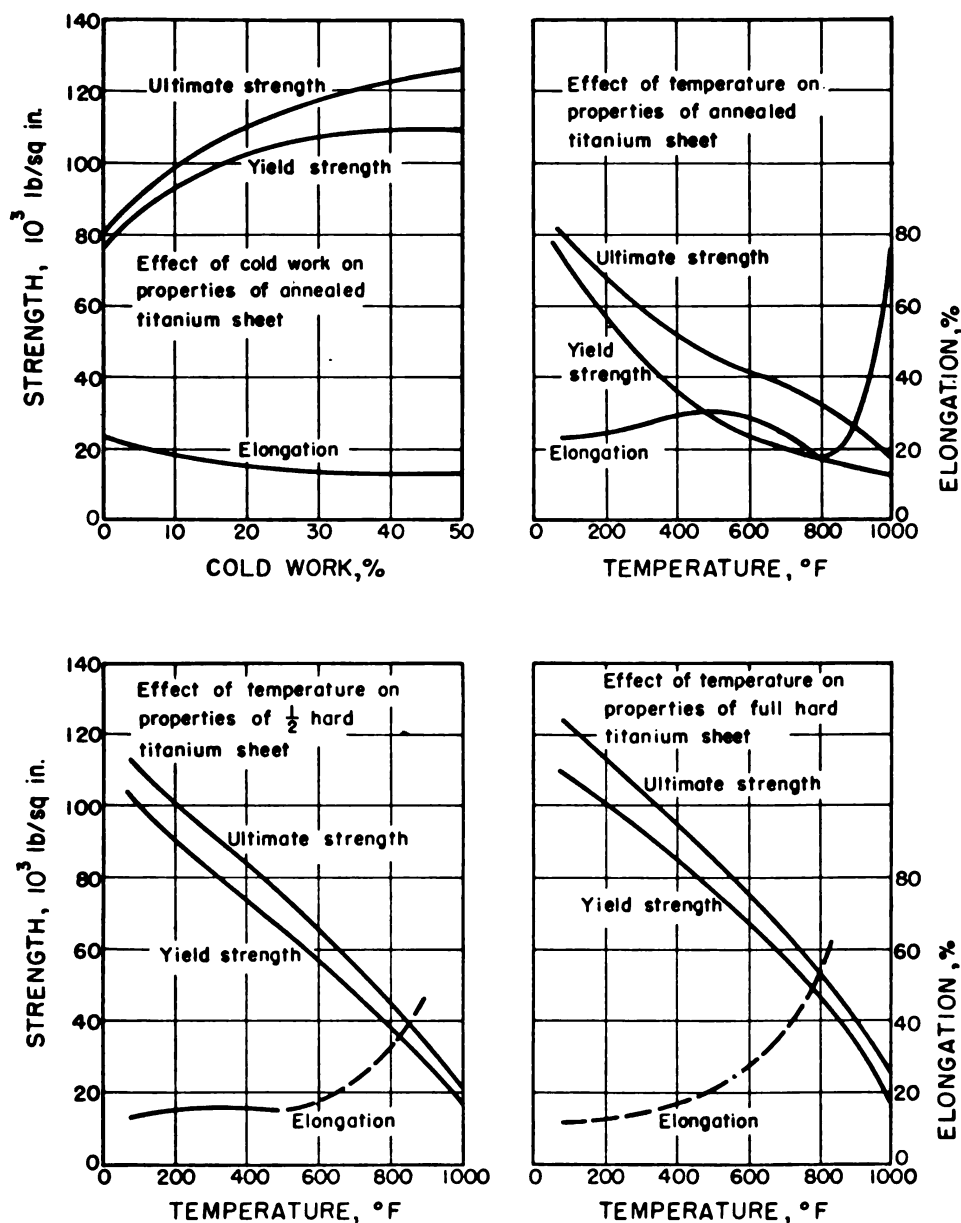


Fig. 1.20.3—The Effect of Cold Work and Temperature on the Properties of Commercial Titanium. Reprinted from Technical Information on Titanium Metal, Remington Arms Company, July 20, 1950.

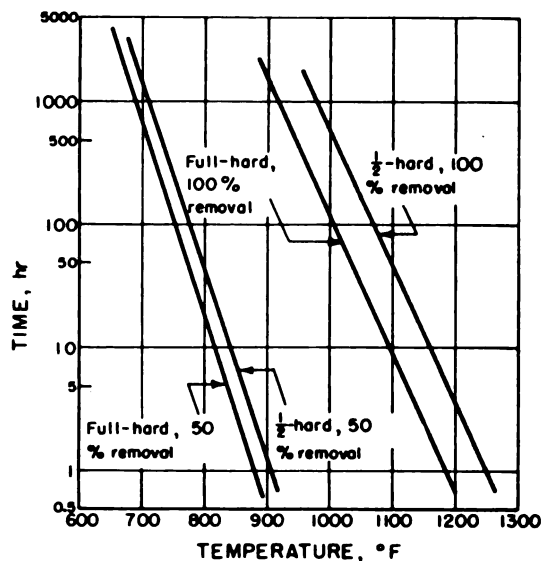
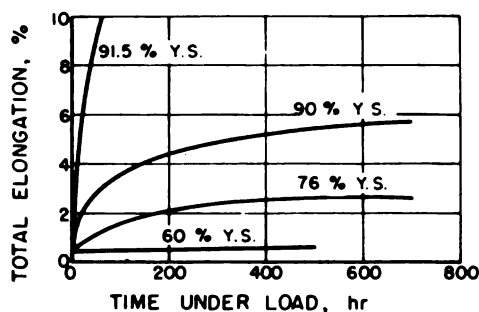
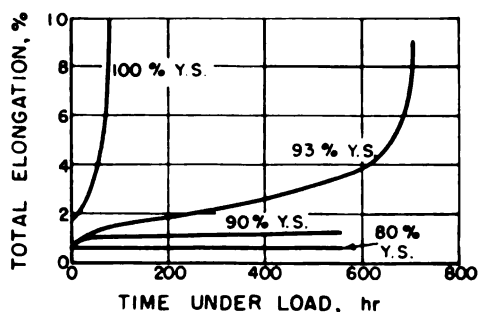


Fig. 1.20.4—Time-temperature Curves for Removing Strain Hardening From Cold-worked Tempers of Titanium. Reprinted from Technical Information on Titanium Metal, Remington Arms Co., July 20, 1950.



Creep of Annealed Titanium at Room Temperature



Creep of Cold Rolled Titanium at Room Temperature

Fig. 1.20.5—Creep Curves for Commercial Titanium. Reprinted from H. Adenstadt, Creep of Titanium at Room Temperature, Metal Progress, Vol 56, 1949.

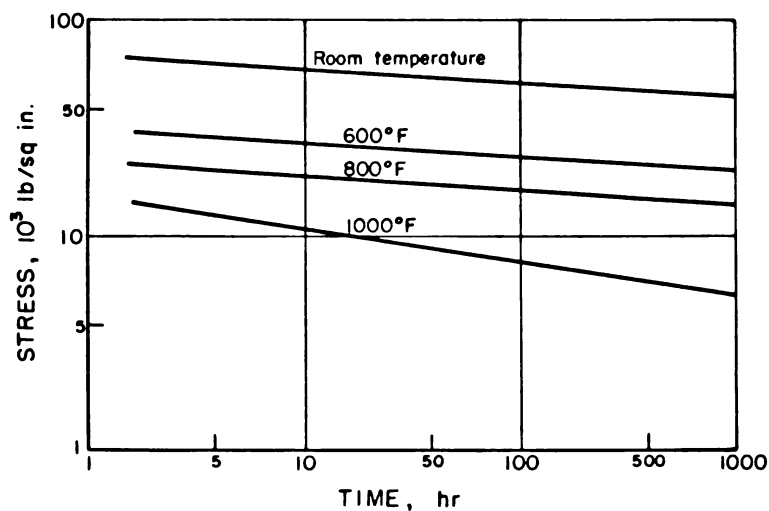


Fig. 1.20.6—Stress-rupture Curves for Commercial Titanium. Prepared from data of Rem-Cru Titanium, Inc.

Table 1.20.8—Stress-to-Rupture Data for
Commercial Titanium in Sodium* at 800° and 1000°F

(Progress Reports 42 and 46, KAPL 298 and 356, Jan. and May 1950.)

Stress, lb/sq in.	Failure time, hr
800°F	
20,000	115
16,000	655
12,000	Still running after 1500
1000°F	
15,000	$\frac{1}{8}$
10,000	2
8,000	6
6,000	86
4,000	325

*Calcium-gettered (oxygen-free)

Figures 1.20.7 and 1.20.8 are stress-rupture curves for titanium alloys Ti-140A and Ti-150A. Figures 1.20.9 and 1.20.10 show the elevated-temperature properties of titanium-base alloys. The properties of most of these alloys are very similar, principally, because all but one alloy are of the same basic type, (i.e., medium quantity of beta stabilizer added). Only the Ti-150A alloy (Ti-5Fe-5Cr-5Mo) is a metastable-beta alloy. This alloy retains its strength somewhat better at elevated temperature than do the other alloys.

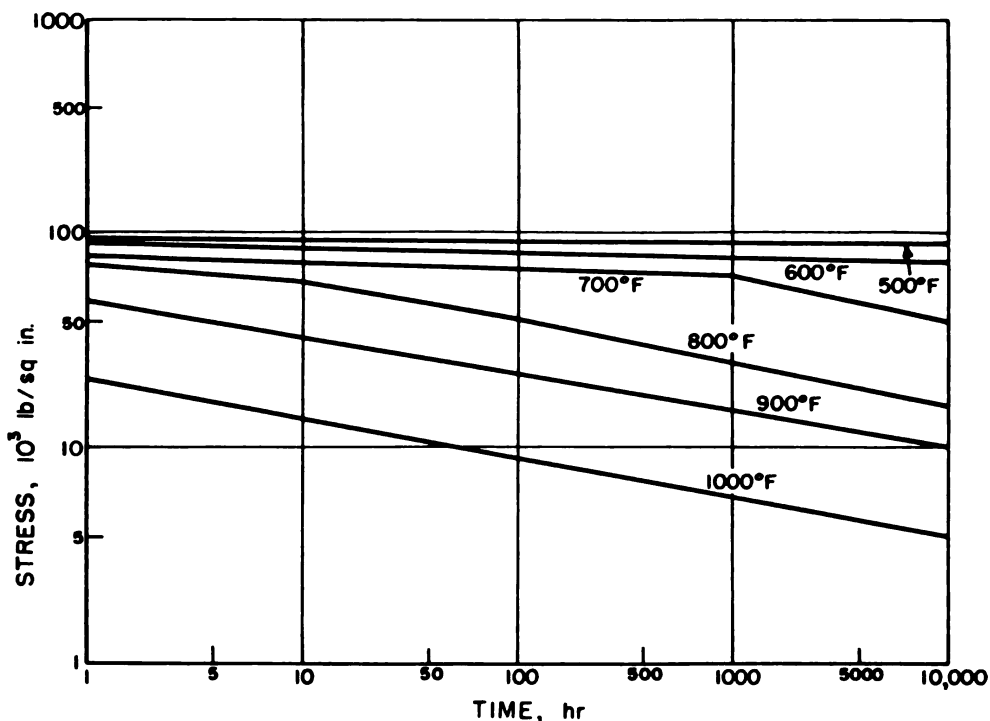


Fig. 1.20.7—Stress-rupture Curves for Ti-140A. Prepared from data of the Titanium Metals Corporation.

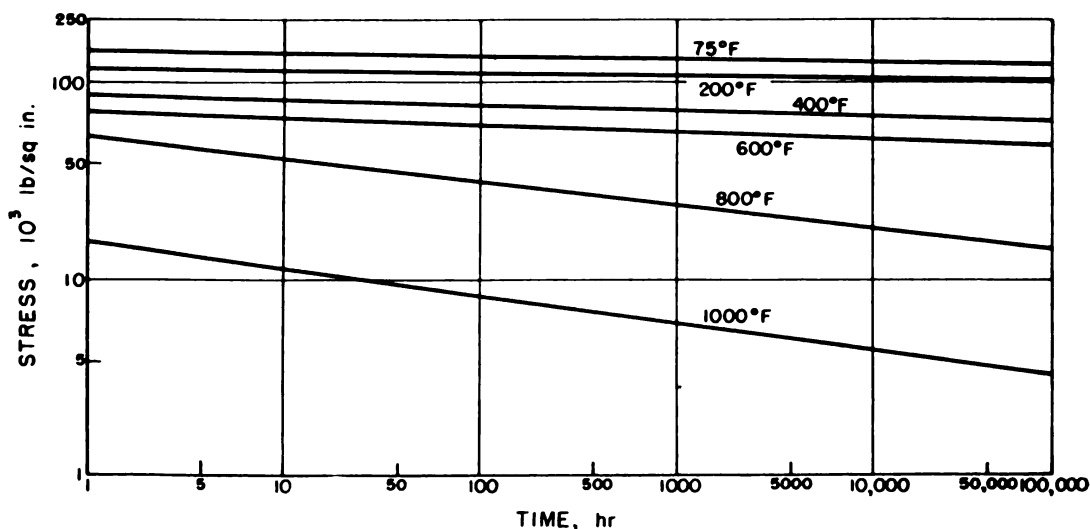


Fig. 1.20.8—Stress-rupture Curves for Ti-150A. Prepared from data of the Titanium Metals Corporation.

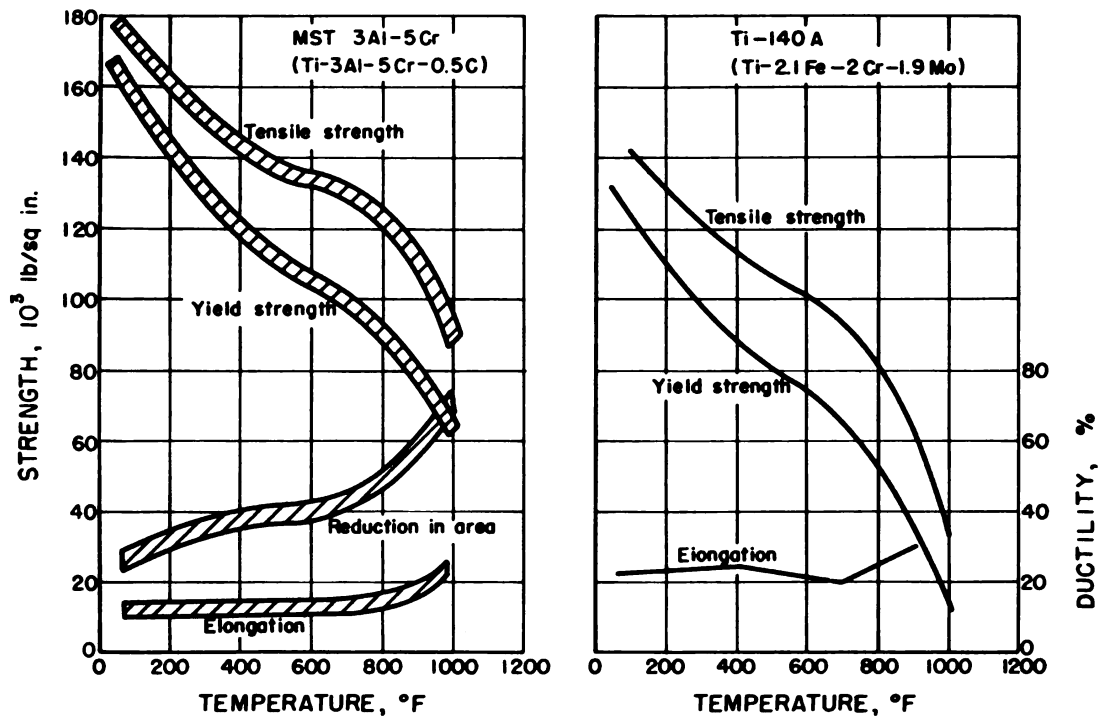


Fig. 1.20.9—Elevated-temperature Properties of Commercial Titanium Alloys. Prepared from data of the Mallory-Sharon Titanium Corporation and Titanium Metals Corporation.

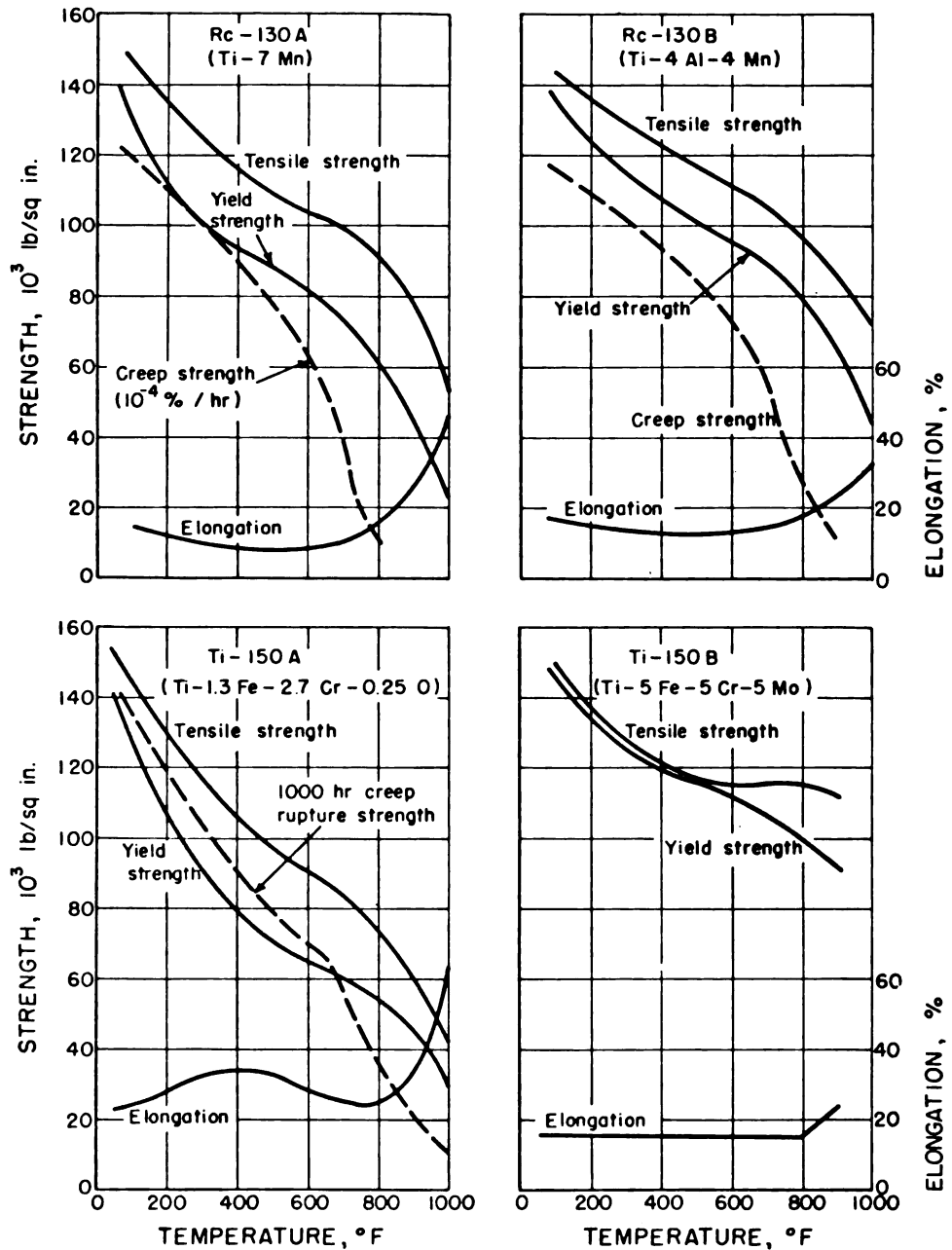


Fig. 1.20.10—Elevated-temperature Properties of Commercial Titanium Alloys. Prepared from data of Rem-Cru Titanium, Inc., and Titanium Metals Corp. of America.

FATIGUE

The fatigue characteristics of titanium are excellent. The endurance limit in flexural fatigue tests has been found to be consistently in excess of 50 percent of the tensile strength. Rotating-beam fatigue curves are shown in Fig. 1.20.11 for notched and unnotched titanium.

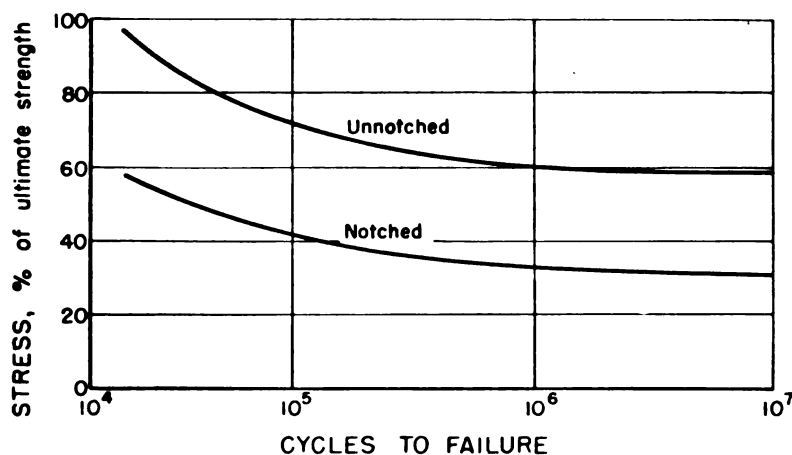


Fig. 1.20.11 — Rotating-beam Fatigue Curves for Annealed Titanium. Prepared from data of Rem-Cru Titanium, Inc.

IMPACT

The toughness of titanium seems to depend on the purity of the metal being tested. The interstitially dissolving elements, carbon, oxygen, nitrogen, and particularly hydrogen, have a detrimental effect on impact properties. Commercial titanium has been reported to have a transition from ductile-to-brittle behavior similar to steel at about 100°F. However, certain lots of magnesium-reduced titanium that are almost free of impurities and iodide-refined titanium have no transition from ductile-to-brittle behavior in impact testing at temperatures down to -320°F. Hydrogen has been found to influence the magnitude of the impact value obtained in high-purity titanium. The higher the quantity of hydrogen present, the lower the impact value. The impact-energy transition curves for commercial titanium and several titanium alloys are shown in Fig. 1.20.12.

MELTING AND CASTING

The melting and casting of titanium and titanium alloys require special techniques because of the high reactivity of titanium with all the known refractory materials. Two types of melting are used to produce titanium today, arc melting and induction melting. Both types of melting are done under an inert atmosphere so that the melt will not be contaminated with oxygen and nitrogen from air,

Arc melting has the advantage that it can be carried out in a water-cooled metal crucible and that no contaminants are picked up from the crucible. The chief disadvantage of this type of melting is that only a small portion of the metal is molten at a time and that the ingot is built up layer by layer. When melting unalloyed titanium, this method is satisfactory, but when melting alloys, there is the possibility of ingot segregation. However,

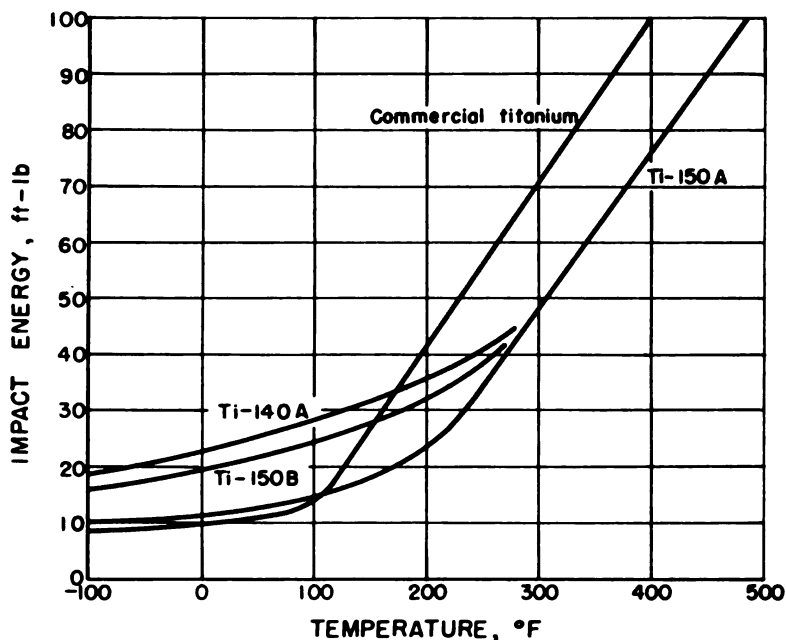


Fig. 1.20.12—Impact-energy Transition Curves for Titanium Alloys. Prepared from data of the Titanium Metals Corporation.

preliminary mixing of alloying ingredients and controlled rates of melting have permitted commercial producers to melt alloys with minimum segregation. Production furnaces embody the principles used in laboratory furnaces, the designs of which have been widely publicized.*

Induction furnaces used for melting titanium are of the high-frequency type. Special adaptations are used to provide protective atmospheres and bottom-pouring mechanisms. The most satisfactory crucible material for induction melting is graphite. Titanium and its alloys dissolve carbon from the crucible walls during melting which is the major disadvantage to induction melting. Carbon has a deleterious effect on the ductility of titanium as discussed later. In production, the carbon content is kept at a minimum by using very short melting times, but still the carbon content ranges from 0.5-0.8 percent. Oxide crucible materials are highly reactive with titanium and cannot be used because of the embrittling effect of dissolved oxygen. The search for a suitable crucible material is continuing.

A melting technique now under development is "skull" melting. In this technique, a "skull" of titanium is built up on the walls of a crucible; this skull remains solid and prevents the molten titanium from being contaminated by the crucible material. An external source of heat, such as a direct or indirect arc, is required, and the metal must be kept under an inert atmosphere. This method has the advantage that the entire melt can be kept molten long enough to obtain intimate mixing of the alloying constituents without crucible contamination.

*See O. W. Simmons, C. T. Greenidge, and L. W. Eastwood, Symposium on Titanium, The Production and Arc-Melting of Titanium, ONR, March 1949, and S. F. Radke, R. M. Sriver and J. A. Snyder, Arc Melting of Titanium, Journal of Metals, Vol 3, 1951.

To date, no titanium castings other than ingots have been made commercially since the present melting methods make the production of castings very difficult. However, intricate castings have been produced on a laboratory scale.

FORMING AND FABRICATION

FORGING AND HOT ROLLING

Structural forms of titanium and its alloys can be produced by conventional forging and rolling techniques used for stainless steels. Forging temperatures should not exceed 1850°F, above which excessive oxygen contamination takes place, and should not decrease below 1300°F, where too much low-temperature forging may cause cracking. Titanium and the commercial alloys can be forged readily in closed dies. The metal flows easily, readily fills the die, and gives good sharp impressions. Flash can be removed without tearing in conventional trimming dies. Such items as turbine blades, rotors, pistons, aircraft landing-gear parts, and other complex shapes are being produced regularly in closed dies. Titanium sheet and rod are produced by hot working. Rolling temperatures between 1300° and 1500°F are generally used.

COLD ROLLING

Cold working can also be used to fabricate sheet, but, since only about 30 to 50 percent reduction can be obtained, frequent anneals are needed. Generally, cold rolling is reserved for a final treatment to produce smooth surfaces or improve the strength properties of the sheet. The effects of cold work can be removed by a 2-hr anneal at 1100° to 1300°F.

EXTRUSION

Extrusion, like drawing of titanium, is hampered by galling and seizing. Although extrusion of titanium has been accomplished experimentally, no commercial extrusions are available. One method used to overcome seizing is based on the Sejournet process which utilizes a glassy lubricant for high-temperature extruding. Other methods are probably under development, but no information is available at this time.

DRAWING AND MISCELLANEOUS TECHNIQUES

Commercial titanium sheet can be formed by drawing, bending, spinning, dimpling, stretch forming, and other similar methods. In general, the formability of titanium can be compared to $\frac{1}{2}$ -hard stainless steel with the exception that the amount of stretch is limited to about 10 percent. Titanium, particularly its alloys, have a high spring-back tendency; consequently, many of the bending operations are done warm (about 500° to 600°F) to eliminate spring-back and cracking. Drawing operations are somewhat difficult to perform because of the galling and seizing tendency of titanium. High press pressures and adequate lubrication are required for deep-drawing parts. Press speeds should be lower than those used for steel, and a draw radius of about 8 times the thickness of the sheet is recommended to prevent cracking. Lubricants for use in drawing operations are still in the development stage. Sulfurized and chloridized polar lubricants, selective surface oxidation, phosphate coating, and copper plating are some of the methods used to prevent galling and seizing.

POWDER-METALLURGY TECHNIQUES

Titanium is well suited to powder-metallurgy techniques as a means of consolidation and fabrication. Titanium powder has excellent green strength; the powder compacts can be

sintered easily; and, after fabrication, the resultant sheet or rod has approximately theoretical density. However, for the production of titanium on a tonnage scale, powder metallurgy cannot compete with melting techniques.

Titanium powder can be produced by grinding the sponge obtained in the Kroll process or from the decomposition of titanium hydride. It is of interest that early experimental work on titanium by the U. S. Bureau of Mines utilized powder-metallurgy techniques. Titanium powder produced by the original Kroll process was compacted at about 50 ton/sq in., sintered for 16 hr in vacuum at 1830°F, and sheath-rolled to final size. These techniques are still applicable today. Subsequently, it was found that satisfactory sheet could be produced by sealing titanium powder in welded metal sheaths and fabricating the assembly at elevated temperatures.

Sheath rolling is necessary because compacted titanium powder has very poor oxidation resistance. Even in the final fabricated form, samples made from powder are very susceptible to elevated-temperature oxidation and embrittlement by contamination which is the major drawback to powder-metallurgy techniques. The normal mechanical properties of powder-metallurgy titanium are about the same as those exhibited by arc-melted titanium.

JOINING

Joining methods can be classified as: welding, brazing, soldering, and riveting. Of these, only riveting is applicable to titanium with no difficulties. Welding, brazing, and soldering all depend on metal fusion and present complications.

RIVETING

Titanium has been riveted to titanium using stainless steel, Monel, and titanium rivets. Stainless steel and Monel rivets require less driving force than do titanium rivets, and since there is little or no galvanic corrosion when using them, they are recommended as rivet material.

WELDING

The problem of welding titanium is mainly that of excluding contaminants from the surfaces to be welded and the welding operation. Therefore, to obtain a satisfactory weld, the surfaces to be welded must be clean and welding must be done in a manner such that no oxygen or nitrogen comes in contact with the fused metal; in addition, the carbon content of the metal to be welded must be less than 0.2 percent. When welded under an inert atmosphere, titanium welds are ductile and have about the same strength as the base metal. A typical setting for automatic arc-welding of titanium sheet is:

Electrode	$\frac{1}{16}$ -in.-diameter tungsten
Gas	Argon
Gas flow	8 cu ft/min
Speed	27 in./min
Current	90 amps D-C, electrode negative
Backing	Argon or metal

Titanium can also be spot welded, resistance seam welded, and flash welded if the surfaces to be welded are clean. Spot welding of titanium requires higher pressures and higher welding currents than low-carbon steel of the same thickness. It is characteristic of titanium spot welds that the penetration is high, generally about 80 percent, but this

does not adversely affect the weld properties. A typical setting for spot welding titanium is:

Sheet thickness	0.022 in.	0.060 in.
Electrode material	Mallory 3	Mallory 3
Electrode force	600 lb	1000 lb
Electrode tip radius	3 in.	3 in.
Squeeze time	40 cycles	40 cycles
Current on	10 cycles	24 cycles
Cooling time	40 cycles	40 cycles
Welding current	6000 amp	6000 amp

Seam welding, like spot welding, is readily adapted to joining titanium. Typical settings for seam welding 0.062-in. titanium sheet are:

Current	9000-10,000 amp
Electrode force	1000 lb
Speed	20 in./min
Welding cycle	12 v on, 6 v off
Electrode	3-in.-radius face

Flash butt welding of titanium can be compared to similar welding of aluminum rather than steel. A short flashing cycle is used to prevent oxidation of the titanium. This is followed by a rapid forging cycle which completes the weld.

The above discussion pertains chiefly to unalloyed titanium having a low-carbon content. Commercial alloys of titanium or commercial titanium containing more than 0.2 percent carbon can be welded by these methods, but the resultant welds generally are brittle. Carbon is definitely detrimental to welds. During the welding operation, titanium carbide freezes out of the liquid metal in networks which embrittle the weld.

Since all of the commercial alloys contain beta stabilizers, they are susceptible to heat-treatment effects. There are two mechanisms which cause weld embrittlement of titanium alloys. Quench hardening or transformation hardening that occurs during the rapid cooling obtained after welding is one cause of embrittlement. This type of hardening probably can be overcome by a post-weld heat treatment. The second, and probably the most important, cause of embrittlement is the segregation that occurs during freezing. This is caused by the wide liquid-solid region in many of the binary systems containing beta stabilizers.

The problems involved in welding titanium alloys do not depend upon welding techniques as the techniques used for commercial titanium can be readily adapted to the alloys. Instead, the problem is one of alloy composition that results in brittle welds. Producers of titanium alloys are well aware of this fact and are developing alloys which will be ductile when welded.

BRAZING AND SOLDERING

Brazing and soldering of titanium are still in the development stage. From the little information available, it appears that some success has been obtained when silver solders (Ag-15Mn, for example) are used, although the alloy layer between the solder and titanium is hard and brittle. No information is available on soldering.

MACHINING

Although the machining of titanium and its alloys has often been compared to that of stainless steel, or in some instances jet-engine alloys, the problems involved are actually

quite different. The machinability of titanium appears to depend on its hardness or strength; the higher the strength, the more difficult it is to machine. Some investigators attributed the machining difficulties to work hardening, but more recent indications are that tool materials alloy with titanium and dull the tool.

The comparison with stainless steel, however, has merit. The type of chip formed when machining titanium resembles that formed with stainless steel. Also, tool designs which have been successful for machining austenitic stainless steels have proven satisfactory for machining titanium and its alloys. Recommended practices for machining titanium and its alloys are:

(1) For roughing cuts; speeds of 45 to 60 surface ft/min (sfm), minimum feed of 0.030 in./rev, and depth of cut twice the minimum feed.

(2) For finishing cuts; speeds of about 70 sfm, minimum feed of 0.015 in./rev, and depth of cut 0.015 in. Slow-speed machining with heavy cuts is, therefore, the recommended practice. Lubricants used in these slow-speed operations are generally cutting oils with added chlorinated solvents such as carbon tetrachloride. It is important to keep the work and tool as cool as possible, liquid carbon dioxide has been used successfully for this purpose. Cutting speeds of more than 300 sfm have been found satisfactory in lathe, milling, drilling, and broaching operations when liquid carbon dioxide is sprayed on the cutting edge of the tool.

In all machining operations, in addition to slow speeds and heavy cuts, it is mandatory that the feed must not be disengaged while the tool is moving in contact with the work. This practice prevents seizing and galling and results in longer tool life.

The grinding of titanium is difficult and expensive because of the high rate of wheel wear. It has been estimated that for each cubic inch of titanium removed by grinding $2\frac{1}{2}$ cu in. of abrasive are used. With such high rates of wheel wear, it is difficult to meet close tolerances. The recommended abrasive is alumina using slow wheel speeds (2000-3000 sfm). Grinding should be done wet to keep the work cool and to prevent burning or explosion of titanium dust.

HEAT TREATMENT

Although titanium undergoes a transformation, no significant change in properties can be brought about by quenching from the beta field, nor are alloys containing alpha stabilizers susceptible to heat treatment effects, either quench hardening or age hardening. Only the alloys containing beta stabilizers are heat treatable.

The similarity between titanium and steels (both undergo allotropic transformations, and in certain alloys martensite can be formed by quenching) has been pointed out by many investigators. Actually, the similarity ends there. Titanium alloys susceptible to martensitic hardening are of the alpha-beta type; that is, they contain moderate quantities of beta-stabilizing elements. The increase in strength or hardness caused by quenching to martensite is not very great, and it is generally accompanied by embrittlement of the alloy. At the present, the most effective known heat treatment for alpha-beta alloys is quenching from within the alpha-beta field. The strength of the two-phase alloy is a function of the quantity of beta phase present; therefore, the higher the alloy is heat treated in the two-phase field, the stronger the alloy.

At this time, no suitable heat treatment has been developed to give titanium alloys improved properties over an alpha-beta anneal. Alloys containing just enough beta-stabilizing element to retain the beta phase by quenching are also hard and brittle. This type of hardening has been called "coherency hardening" or "incipient-transformation hardening." It is possible that embrittlement of martensitic hardening is not caused by the martensite needles, which are a supersaturated alpha phase, but rather by coherency hardening of the retained beta phase in the interstices of the alpha needles.

Titanium alloys containing beta-stabilizing elements are also susceptible to age hardening. In most beta-stabilized systems the beta phase is either not stabilized to room temperature until very high contents are reached, or it undergoes a eutectoid reaction. Thus, in alloy compositions of interest, the beta phase in any alloy will precipitate alpha phase at relatively low temperatures with the result that the alloy becomes hard and brittle. It is unfortunate that the age-hardening temperature range is also the probable service temperature range for titanium alloys, 400° to 800°F. Age hardening is therefore a disadvantage rather than an attribute of these alloys, and steps must be taken to overcome the embrittling effect. This can be done by rejecting as much alpha phase from the beta phase as possible during the annealing operation. One recommended treatment is an anneal at 1400°F followed by furnace cooling to 1100°F and air cooling to room temperature. Alternatively a stepwise anneal starting at about 1400°F and ending at 1100°F can be used.

Since hardness is a function of the oxygen and nitrogen contamination, it is possible to surface harden titanium by heating it in air. In this way, controlled surface hardness and core depths can be obtained. Figure 1.20.13 shows this effect on the surface hardness of titanium.

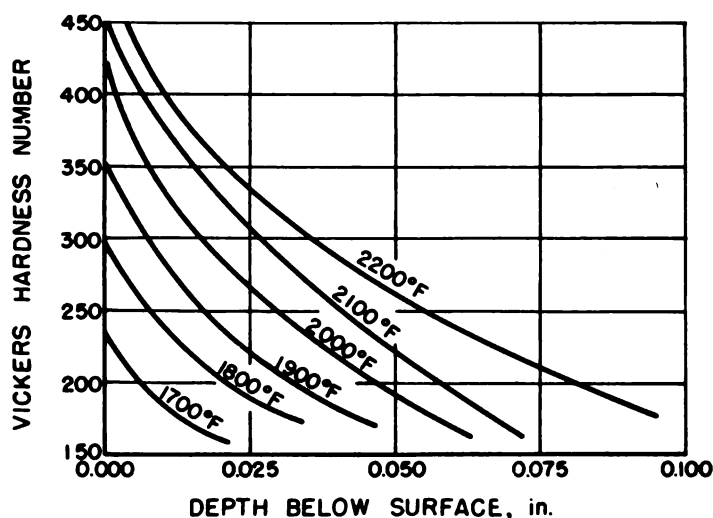


Fig. 1.20.13—Surface Hardening of Titanium by Heating in Air for 1 Hour at Temperature. Reprinted from Handbook on Titanium Metals, 4th Edition, Titanium Metals Corporation, July 15, 1951.

In general, the heat treatability of titanium alloys has so far proven to be a detriment. However, as the metallurgy of titanium alloys is advanced, heat treatments of value may be developed.

CORROSION BEHAVIOR

One of the attributes of titanium is its resistance to chemical attack in many environments, particularly in the presence of chlorides and under oxidizing conditions. It is resistant to oxidizing acids such as nitric acid and aqua regia, to dilute concentrations of sulfuric and hydrochloric acid, and to most organic acids at room temperature. It is attacked by hydrofluoric and phosphoric acids at room temperature and by concentrations of over 5 percent hydrochloric acid. Titanium resists attack by dilute alkalis but is at-

tacked by moderate concentrations of the alkalis. It has excellent resistance to attack by sea water, marine atmospheres, and many boiling dilute solutions of chlorides.

When titanium is attacked, corrosion is of a general, uniform nature with no localized pitting or intergranular attack. Little difference in corrosion resistance has been found between annealed and cold-rolled titanium, although when the latter is subjected to severe corrosion, an end-grain attack typical of other rolled metals occurs.

Titanium has been placed between Inconel (passive) and Monel in the galvanic series for various metals and alloys in sea water. Thus, titanium is cathodic to most of the other structural metals. Although titanium is generally unattacked in a couple with other materials, the corrosion of the more active metals is accelerated considerably.

The corrosion resistance of titanium can be attributed to the formation of a passive oxide film, which explains its resistance to oxidizing environments. This oxide film affords protection only at low temperatures with the result that titanium is not oxidation resistant at elevated temperatures. Titanium oxidizes when heated in air at temperatures as low as 480°F, and the oxidation rate increases as the temperature is increased. Figure 1.20.14

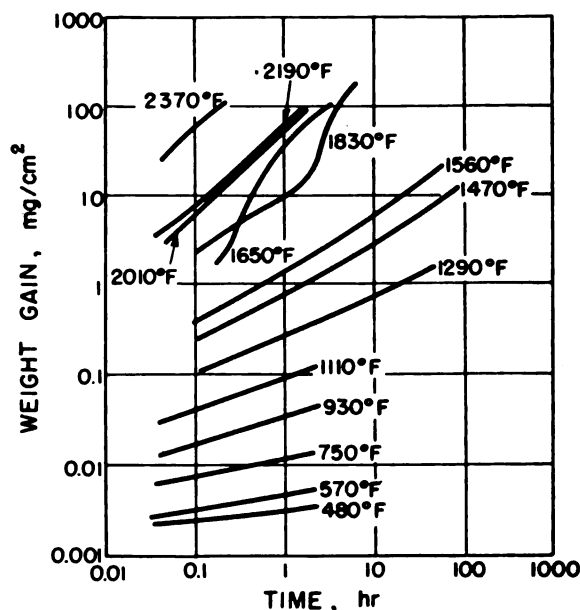


Fig. 1.20.14—Weight Gain of Titanium Heated in Air at Various Temperatures. Reprinted from P. H. Morton and W. M. Baldwin, Jr., *The Scaling of Titanium in Air*, Trans. ASM, 1952.

shows some weight gain versus time curves for titanium heated in air at several temperatures between 480° and 2370°F. It should be noted that there is a large difference in oxidation rates between 1560° and 1650°F and that the rates at temperatures of 1650° to 2370°F are very high and close together. This difference may be attributed to the difference in crystal structure of titanium between 1560° and 1650°F. The close-packed-hexagonal form of titanium exists at temperatures below 1625°F and the body-centered-cubic form at temperatures above 1560°F.

Not only does titanium oxidize rapidly at elevated temperatures, but it also absorbs oxygen and nitrogen in solid solution. The rate of diffusion of these interstitial elements

into titanium depends on the temperature of exposure, and consequently, the length of time that titanium can be exposed to air depends on the thickness of the metal and the temperature. For example, a 0.040-in. sheet becomes embrittled when exposed for several hours at 1500°F; however, the same sheet can be exposed for at least 500 hr at 1050°F with no change in properties. At the other extreme, 0.015-in. titanium sheet has withstood a 2000°F flame test for 15 min and has been accepted as satisfactory firewall material by the Naval Bureau of Aeronautics.

In elevated-temperature water, titanium has been found to have excellent corrosion resistance. Titanium, as an intermediate metal between copper electrodes and zirconium-clad molybdenum, was found to be corrosion resistant in 500°F water.

Titanium appears to be of limited value as a container for liquid metals. Mercury and calcium-gettered (oxygen free) sodium are the only liquid-metals in which the corrosion resistance of titanium is outstanding. In all others, the rate of attack is too great to permit the use of titanium.

In a one-month static service test at KAPL, commercial titanium in calcium-gettered sodium at 932°F was essentially unattacked showing an average weight gain of 0.23 mg/(cm²)(mo) and only slight discoloration.

The corrosion properties of titanium alloys have not been investigated to any great extent. The general statement that the corrosion behavior of titanium alloys is similar to that of commercial titanium is being used principally because no experimental data are available. Recently, work at the U. S. Bureau of Mines has shown that small additions of zirconium (as little as 3 percent) to titanium greatly increase the corrosion resistance of titanium in acid media. Also, they have found that an alloy of titanium containing 1.9 percent chromium and 0.9 percent iron is slightly less resistant to acids than commercial titanium.

METALLOGRAPHY

The fact that titanium has two allotropes gives rise to many interesting, if not complex, structures. High-purity titanium when fabricated and annealed in the alpha field has an equiaxed-grain structure, the grain size of which is dependent on the annealing treatment. When high-purity titanium is quenched from the beta field, the structure is no longer equiaxed, as the beta phase cannot be retained by quenching, but it consists of large serrated grains of alpha formed during the transformation. These are the two basic types of structures found in titanium. They can be altered by impurities present and alloying additions.

For several years, titanium metallographers have been plagued by a so-called "X-phase" which was found in alpha titanium and is now identified as titanium hydride particles which precipitate at low temperatures.

In a binary system containing an alpha stabilizer such as oxygen, nitrogen, or aluminum, the alpha structure resembles that of unalloyed titanium. An alloy heat treated in the alpha-beta field will have a structure consisting of alpha grains in a matrix of transformed beta, while the same alloy heat treated in the beta field will consist entirely of transformed beta. The type of transformed beta obtained depends on the composition of the alloy, or more specifically, the width of the alpha-beta field. If the alpha-beta field is narrow, the transformation structure will be the serrated type, and if the alpha-beta field is wide, the transformation structure is a basket-weave type. Generally, commercial-purity titanium when quenched from the beta field has a basket-weave structure because the oxygen and nitrogen present cause a wide alpha-beta region.

Alloys containing beta stabilizers can have many different microstructures. An alloy containing a moderate amount of a beta stabilizer, fabricated and annealed in the alpha-beta field, has an equiaxed two-phase, alpha-beta structure. The same alloy quenched from

the beta has a martensitic structure which, if subsequently annealed, has an acicular type of alpha-beta structure. At high-alloy contents, the beta phase can be retained by quenching and has a large-grained equiaxed structure. Subsequent, low-temperature aging or slow cooling from the beta field causes the precipitation of alpha from the beta.

ALLOYS OF TITANIUM

The commercial grades of titanium have shown much promise as structural materials. However, like other structural metals, titanium can be alloyed to produce much more outstanding properties. During the past five years, considerable research has been done and is continuing on the exploration of the alloying mechanisms, and although only a handful of alloys have been commercialized to date, the future looks promising for the commercialization of many more alloys.

In general, the alloying elements which can be added to titanium can be categorized as follows:

(1) Elements which have a higher solubility in the alpha or low-temperature phase and which raise the transformation temperature of titanium are called alpha stabilizers.

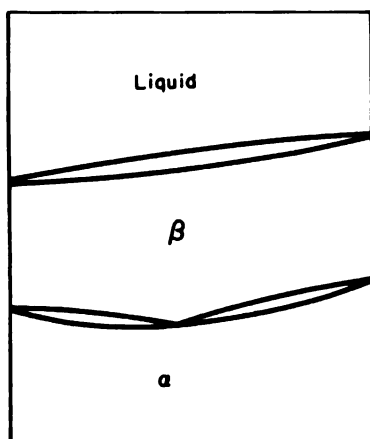
(2) Elements which have a higher solubility in the beta or high-temperature phase and which lower the transformation of titanium are called beta stabilizers.

(3) Elements which do not dissolve to any great extent in titanium and which form inter-metallic phases are called compound formers.

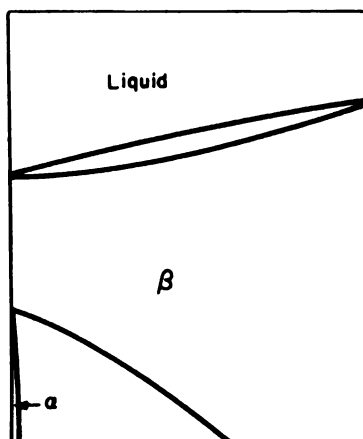
For these elements which dissolve in titanium, the general types of equilibrium diagrams are shown in Fig. 1.20.15. All of the transition elements whose diagrams are known can be classified as beta stabilizers; this includes zirconium which, although completely soluble in both alpha and beta titanium, lowers the transformation temperature and fits the broad definition. The common interstitial contaminants of commercial titanium, i.e., carbon, nitrogen, and oxygen, are alpha stabilizers whereas the substitutional contaminant, iron, is a beta stabilizer. Therefore, the wide transformation range found in commercial titanium, which brackets the accepted value of 1620°F, can be attributed to the influence of the four major contaminants.

It is possible to generalize on the effects on the mechanical properties of titanium of the three basic types of alloying additions. Those elements which are alpha stabilizing strengthen titanium by solid-solution hardening. Alpha-stabilized alloys are not susceptible to heat treatment, are generally weldable, and do not become embrittled in elevated-temperature-service conditions. The increase in strength caused by the alpha additions varies with the alloying addition, and generally, the ductility decreases progressively as the strength increases. The alpha additions, therefore, are probably most suitable for producing moderate-strength alloys which are isotropic in the annealed condition. Alpha additions may also be used in alpha-beta alloys to enhance the properties of the alpha phase of the two-phase alloy.

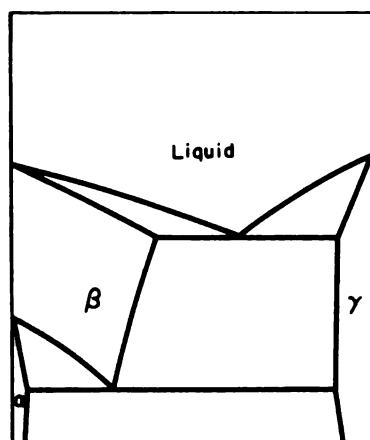
Beta-stabilizing additions are the most versatile of all additions to titanium. When added in small or medium quantities, the resultant alloy can be processed to have a two-phase alpha-beta structure or can be heat treated to have a martensitic structure. The alpha-beta structure which results from fabricating and annealing at temperatures within the two-phase region provides an alloy with the highest combination of strength and ductility found in titanium-base alloys to date. These alloys can be processed to be stable at moderately elevated temperature, can be formed by bending operations, are somewhat anisotropic in properties, and generally cannot be welded without embrittlement. These same alloys, if quenched or rapidly cooled from the beta field, have a structure similar to martensite in steel. In this condition, the alloys are generally much less ductile than in the alpha-beta condition, cannot be formed by bending, and are not stable at elevated temperatures. The instability at elevated temperatures is caused by a precipitation or transformation of alpha



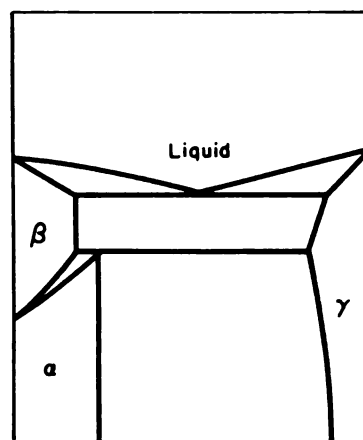
Alpha and Beta Isomorphous
Zirconium
Hafnium*



Beta Isomorphous
Vanadium
Niobium
Molybdenum
Tantalum



Beta Eutectoid
Hydrogen Iron
Beryllium Cobalt
Silicon Nickel
Chromium Tungsten
Manganese Uranium
Silver*



Terminal Alpha
Carbon Tin*
Nitrogen Antimony*
Oxygen Indium*
Aluminum Lead*
Bismuth*

* Diagram not established but probably of the type shown

Fig. 1.20.15—Hypothetical Titanium-base Binary Diagrams.

phase from the beta phase which embrittles the alloy. If larger quantities of a beta stabilizer are added to titanium, a metastable or stable beta alloy can be produced. A metastable beta alloy is one in which the all-beta microstructure is obtained by quenching from the beta field. Such an alloy is generally unstable at moderately elevated temperatures. A stable beta alloy can be produced only by the use of additions that will lower the transformation of titanium to room temperature or to a temperature where diffusion is inoperative. These alloys are thermally stable and are isotropic. However, so much beta-stabilizing addition is required to produce them that they lose much of the advantage of the low density of titanium and generally contain large quantities of strategic materials.

The elements which form compounds with titanium do not afford any significant improvement in properties and if present in large enough quantities cause embrittlement. Unless compound formers are found to provide special properties, such as improved machinability, it is doubtful that they will be of value in titanium metallurgy.

INTERSTITIAL ALLOYING ADDITIONS

Previously, it was stated that the affinity of titanium for the interstitial alloying additions, carbon, oxygen, nitrogen, and hydrogen, demanded extravagant precautions in refining and melting operations. Therefore, the functions and consequences of alloying with the interstitial elements should be understood.

Both oxygen and nitrogen have very high solubilities in alpha titanium, and oxygen (and probably nitrogen) extends the alpha field up to the melting range. Carbon, on the other hand, has a low solubility in the alpha field and a much lower solubility in the beta field. Hydrogen, unlike carbon, oxygen, and nitrogen, stabilizes the beta phase of titanium down to a eutectoid temperature somewhat below 750°F.

The detrimental effect of oxygen and nitrogen on the mechanical properties of titanium is caused by solid-solution hardening. The strength or hardness of impure titanium is a direct function of the oxygen and/or nitrogen content and the purity of titanium is often designated by using hardness as a measure of the combined oxygen and nitrogen content. In conjunction with the strengthening and hardening effect, oxygen and nitrogen have an embrittling effect that can be disastrous to titanium. Carbon, because of its low solubility, does not have the strengthening or embrittling effect of oxygen and nitrogen. When carbon is present in excess of the solid-solution limit, carbides are formed which cause some decrease in ductility and formability. However, in the cast condition, the carbides are present in networks which are definitely embrittling. Thus, the presence of carbides is particularly detrimental when titanium is being welded.

Small controlled amounts of carbon, oxygen, and nitrogen, however, can be tolerated in and are beneficial to titanium. Many alloys, including commercial titanium, receive much benefit from the presence of these elements in small quantities. It can be seen from the curves of Fig. 1.20.2 that nitrogen and oxygen have potent strengthening effects, nitrogen additions being the most potent and also the most detrimental to ductility. The tolerance of high-purity titanium for oxygen is quite high, and in many alloys, oxygen is purposely added to boost the alloy's strength without severely damaging ductility. Carbon in solid solution (i.e., up to about 0.25 percent) is also beneficial to strength and can be used as an auxiliary strengthening addition. However, because of its adverse effect on weldability, the upper limit generally is about 0.2 percent.

Hydrogen, at first glance, appears to be an innocuous addition to titanium. When present in small quantities, it has no apparent effect on strength or ductility. However, it has recently been discovered that, although the solubility of hydrogen in alpha titanium is about 8 atomic-percent (0.17 weight-percent) at the eutectoid temperature (about 615°F), the solubility is very low at lower temperatures and that titanium hydride precipitates at the low temperatures with a detrimental effect on impact properties. In large quantities, hydrogen does embrittle titanium. Hydrogen can probably be picked up in titanium from

pickling solutions, descaling baths, and water vapor in otherwise inert atmospheres used in the refining or melting operations. It is never intentionally added to titanium.

SUBSTITUTIONAL ALLOYING ADDITIONS

The currently available commercial alloys of titanium contain one or more of the following alloying additions in addition to the interstitial elements present in commercial titanium: aluminum, chromium, iron, manganese, molybdenum, and vanadium. Of these six elements, only aluminum is an alpha stabilizer; all others stabilize the beta phase. Aluminum is used principally in combination with one of the other alloying ingredients to strengthen the alpha phase of a two-phase alloy. When added alone, aluminum has a strengthening effect similar to oxygen and nitrogen, but it too has only a limited useful range because of its embrittling action when present in quantities greater than 8 percent. There is, then, a similarity between aluminum and oxygen or nitrogen. The equilibrium diagrams are also similar in that aluminum is the only known substitutional solute which raises the transformation temperature of titanium.

Iron, manganese, chromium, and molybdenum have been called the "big four" alloying additions to titanium. All four elements are beta stabilizers, although only molybdenum and chromium form continuous series of solid solutions with beta titanium. Iron and manganese have considerable solubility in beta titanium but also form intermetallic compounds with titanium. The beta phase in systems containing chromium, iron, or manganese decomposes eutectoidally, whereas in the titanium-molybdenum system, the beta phase is stabilized to room temperature and below at high molybdenum contents.

Actually, all of these systems can be considered as basically the same type in the titanium-rich region because the eutectoid reaction is so sluggish as to be unimportant. Therefore, the general effects of beta stabilizers on mechanical properties can be summarized for all of these systems.

There are two basic types of alloys available in a beta-stabilized system: the alpha-beta type and the metastable beta type. The alpha-beta type contains moderate quantities of a beta-stabilizing element with or without an auxiliary addition of an alpha-stabilizing element. The alpha-beta alloy obtains its strength from the strengths of the two phases present. In general, the beta phase is the stronger of the two phases, but the alpha phase can be strengthened by the addition of an alpha stabilizer, such as oxygen or aluminum. The alpha stabilizer presumably distributes itself in the alpha phase, thus strengthening the weaker of the two phases. This type of alloy is a ductile, strong, and stable alloy when properly annealed in the alpha-beta field. The beta-type alloy contains relatively large quantities of a beta stabilizer and depends for its strength upon the solid-solution hardening of the beta phase. In the beta-quenched condition, these alloys are also strong and ductile but are susceptible to age-hardening embrittlement in the service temperature range from 400° to 1000°F unless given a suitable stabilizing treatment. Heat treatment effects, which play an important part in the metallurgy of beta-stabilized titanium alloys, are discussed earlier in this chapter.

In systems where the eutectoid reaction is not sluggish, such as the titanium-copper and titanium-nickel systems, the alloys obtained do have the good properties found in other beta-stabilized alloys. In general, the ductility is much poorer when sufficient quantities are added to get strengths comparable with other alloys.

SELECTED READING LIST

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CHAPTER 1.21

Tungsten

R. B. Fischer

ABUNDANCE AND AVAILABILITY

Tungsten is considered a rare element in comparison with the abundance of other useful elements. Nevertheless the amount of tungsten used in the United States in recent years has ranged from 5,000,000 to 20,000,000 lb per year.

The world ore reserves are thought to be on the order of 2 billion pounds of contained tungsten. Of this quantity, about 300,000,000 lb is in non-Communist areas. There are estimated to be about 60,000,000 lb of contained tungsten in South America and about the same amount in the United States. These are rough estimates that include submarginal ores and are based on 100 percent recovery.

Tungsten prices have varied widely. Currently (May 1952) the prices are as follows:

Ore	\$ 4.00/lb contained tungsten
Ferrotungsten	5.22/lb contained tungsten
Tungsten powder	7.75/lb
0.5-in. swaged rod	16.00/lb
.004-in. sheet	16.00/lb

EXTRACTION AND PURIFICATION

Because most tungsten ores are of low grade, concentration methods are used to obtain a product containing more than 60 percent WO_3 . Purified WO_3 is prepared from the ore concentrates by mechanical and chemical treatments. The kind of treatment used depends on the characteristics of each particular ore. The purified WO_3 is reduced by hydrogen to tungsten metal powder of high purity. For the production of tungsten powder of lower purity, WO_3 is reduced by carbon or hydrocarbons. Table 1.21.1 gives the typical purity of various forms of tungsten.

Table 1.21.1 — Typical Purity of Tungsten Products*

Tungsten oxide (WO_3)	98+ percent WO_3
Tungsten (carbon-reduced powder)	98+ percent W
Tungsten (hydrogen-reduced powder)	99.5+ percent W

*Analytical data are not generally available for the impurity elements, such as rare earths, in tungsten since these impurities vary from one lot or producer to another

PHYSICAL AND CHEMICAL CONSTANTS

Table 1.21.2 gives selected physical and chemical constants of tungsten.

Table 1.21.2 — Physical and Chemical Constants of Tungsten

Thermal-neutron absorption cross section, barns/atom	19.2 ± 1.0
Density,* gm/cm ³	
Bars presintered at 1400°C	9.9
Drawn wire	19.2
Melting point, °C	3395 ± 15
Boiling point, °C	5930
Heat of fusion, cal/gm	61
Heat of vaporization, cal/gm	1183
Vapor pressure,†	
log vapor pressure = -42,000T ⁻¹ (0.146 log T - 0.164T + 9.84)	
Specific heat,‡ cal/(gm)(°C)	
20°C	0.032
1000°C	.036
Enthalpy, 25°C, cal/gm	1102
Entropy, 25°C, cal/(mole)(°C)	
Condensed phase	8
Gaseous phase	41.5
Electrical resistivity, μohm-cm	
20°C	5.5
750°C	25.5
1200°C	40
2400°C	85
Temperature coefficient of resistivity, per °C	
0° to 170°C	5.1 × 10 ⁻³
Coefficient of linear thermal expansion, per °C	
27°C	4.44 × 10 ⁻⁶
1027°C	5.19 × 10 ⁻⁶
2027°C	7.26 × 10 ⁻⁶
Thermal conductivity,§ cal/(sec)(cm)(°C)	
-183°C	0.46
0°C	0.40
100°C	0.39
1250°C	0.28

$$* \text{Gm/cm}^3 \times 62.43 = \text{lb/cu ft}$$

$$† T = ^\circ\text{K}$$

$$‡ \text{Cal/(gm)(}^\circ\text{C)} \times 1 = \text{Btu/(lb)(}^\circ\text{F)}$$

$$§ \text{Cal/(sec)(cm)(}^\circ\text{C)} \times (2.419 \times 10^2) = \text{Btu/(hr)(ft)(}^\circ\text{F)}$$

CRYSTALLOGRAPHY

STRUCTURE

The ordinary crystal form of tungsten (β) is body-centered cubic. A face-centered cubic form (α), in which the atoms have two sets of special positions, may be formed by the electrolysis of fused tungstates. If this modified form is heated above 700°C, it reverts irreversibly to the simple body-centered cubic form.

LATTICE CONSTANTS

The lattice constants of β -tungsten are as follows:

a_0	3.1647 Å (25°C)
Atomic volume	15.848 Å ³
Closest approach of atoms	2.7407 Å
Atomic radii	1.41 for coordination number 12
	1.37 for coordination number 8

The lattice constant of α -tungsten is $a_0 = 5.048$ Å.

HEALTH HAZARDS

Tungsten does not constitute an important health hazard. However, personnel should avoid inhalation of large amounts of tungsten dust.

HANDLING AND STORAGE

Tungsten is likely to be brittle at room temperature or at lower temperatures and therefore requires careful handling to avoid fracture.

If tungsten is in the form of finely divided powder, it may be pyrophoric in air. In other than powdered form, tungsten is not affected by air at room temperature. To retain the high purity of fine tungsten powder, it should be protected from moisture in the air. Hydrogen-reduced tungsten powder may retain some absorbed hydrogen, which constitutes a minor hazard.

MECHANICAL PROPERTIES

The mechanical properties of tungsten, like those of other metals, are largely dependent on the previous history of the particular lot of metal. By the use of special process techniques, tungsten can often be tailored to meet given requirements.

TENSILE AND COMPRESSION PROPERTIES

The tensile strength of sintered rods (0.25 in. diameter) of tungsten is about 18,000 lb/sq in. Swaging increases the tensile strength to about 215,000 lb/sq in. for 0.026 in.-diameter rod. The swaged rod when drawn to 0.018 in.-diameter wire has a tensile strength of 264,000 lb/sq in. The tensile strength increases with further reduction by drawing until values as high as 590,000 lb/sq in. are obtained for wire about 0.0014 in. in diameter. Fine tungsten wire has the highest strength of any known material.

The tensile strength of tungsten wire is lowered when the wire is recrystallized.

The tensile strengths of a typical 0.024 in.-diameter wire at various temperatures are given in Table 1.21.3.

The compressibility of tungsten is about 1.67×10^{-3} ton/sq in., the smallest value for all the metals.

MODULUS OF ELASTICITY

The Young's modulus of elasticity for tungsten is about 50×10^6 lb/sq in.

Experiments have indicated that, as tungsten wire is progressively drawn to finer sizes,

the elastic modulus increases from 12.8×10^6 to 55×10^6 lb/sq in. The fact that the modulus varies probably is the result of changes in crystal orientation texture. The low initial modulus reflects fabrication variables, such as amount of sintering and pressing.

Table 1.21.3 — Tensile Strength of a 0.024 in.-diameter Tungsten Wire at Various Temperatures

Ultimate tensile strength, lb/sq in.	Temperature, °F
250,000	70
190,000	750
130,000	1470
71,000	2190
28,000	3270

HARDNESS

Tungsten is a relatively hard metal. Sintered bars of tungsten have a hardness of about 255 Vickers. Swaged rods have hardnesses as high as 488 Vickers.

As tungsten is progressively cold worked, the metal increases in hardness as indicated below:

Sheet	0.04 in. thick	45 Rockwell C
Sheet	.01 in. thick	67 Rockwell C
Rod	.25 in. diameter	37 Rockwell C
Rod	.10 in. diameter	40 Rockwell C

The hardness of cold-worked tungsten is reduced slightly when the metal is annealed. Hardnesses of tungsten at various temperatures are given in Table 1.21.4.

Table 1.21.4 — Hardness of Tungsten at Various Temperatures

Temperature, °F	Brinell hardness, 3000-kg load
-310	465
-140	361
20	306
68	262
550	126
970	100
2100	62
2960	40

ELONGATION

The tensile elongation of cold-worked tungsten ranges from 0 to 4 percent. The metal is generally brittle when fully recrystallized. Single-crystal thoriated wire has an elongation of about 20 percent.

The elongation of tungsten wire increases slightly with increasing temperature up to about 2200°F.

REDUCTION OF AREA

The reduction in area of tungsten is decreased as the tensile strength is increased by cold work, as shown in Fig. 1.21.1.

After recrystallization, commercial tungsten may have no measurable reduction in area.

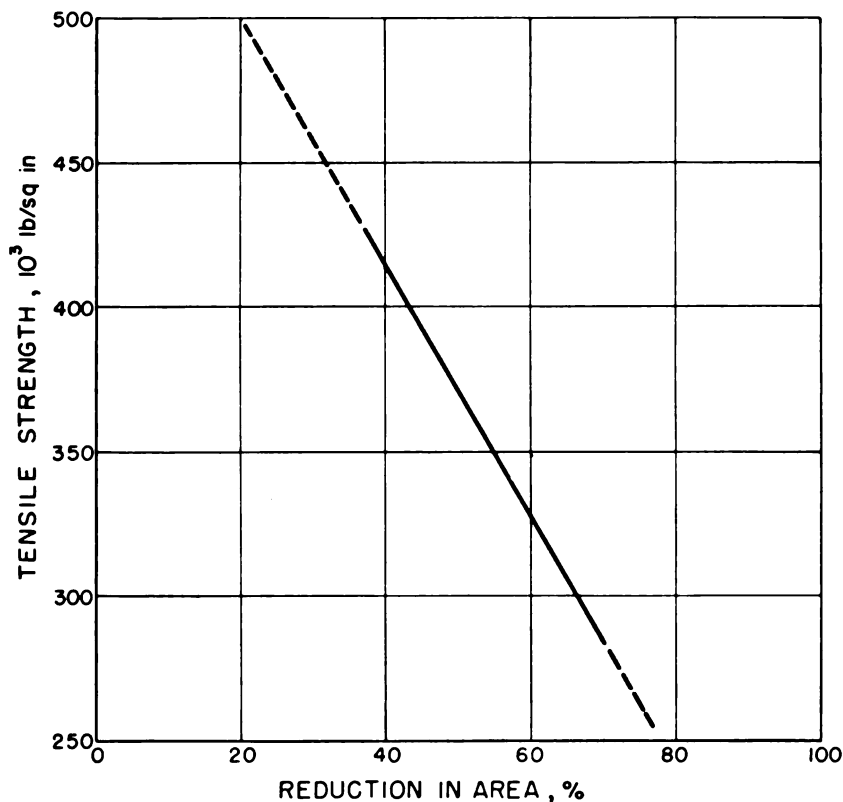


Fig. 1.21.1 — Reduction of Area and Tensile-strength Relation for Tungsten Wire. Reprinted from C. J. Smithells, "Tungsten," 3d edition, Chapman & Hall, Ltd., London, 1952.

CREEP

As fine wire, tungsten retains rigidity at high temperatures better than any other metal. No creep or creep-rupture data are generally available because the uses for tungsten to date have not required the determination of these engineering data to any extent.

TORSIONAL BEHAVIOR

The moduli of torsion of tungsten are as follows:

- 12.8×10^6 to 31.3×10^6 lb/sq in. at 68°F (depending on crystal orientation texture)
- 10.0×10^6 lb/sq in. at 1340°F
- 4.4×10^6 lb/sq in. at 3140°F

MELTING AND CASTING

Because of its high melting point, little work has been done on the melting and casting of tungsten.

Tungsten has been melted as droplets from arc electrodes and from resistance-heated bars. High-frequency current has been used to fuse tungsten in water-cooled quartz, copper, or silver. Recently the vacuum-arc method has been used to make tungsten ingots. No important commercial development of melting and casting tungsten has been made, although it has been demonstrated that forgeable arc-melted ingots can be prepared.

FORMING AND FABRICATION

EXTRUSION

Tungsten filaments were originally prepared by the extrusion of a mixture containing tungsten powder. This process was succeeded by the swaging and drawing technique.

DRAWING

After sintered tungsten bars are swaged to about 0.04 in. diameter, the resulting rods can be drawn to finer sizes. The rods are heated and drawn on a chain bench to about 0.028 in. diameter. At this stage the wire has sufficient ductility to permit coiling and use of power-driven reels. Drawing temperatures are reduced gradually from 1830 to 750°F as the wire becomes progressively finer in size.

ROLLING

With care, sintered or swaged tungsten can be rolled. High temperatures (1830°F) are used in the early stages of rolling. The ductility of the metal is increased by the rolling operation. There is a tendency for the metal to split.

Because of oxidation, it is difficult to roll tungsten to thicknesses less than 0.004 in. by ordinary methods. However, 0.00012 in. sheet has been produced by cladding tungsten with iron.

FORGING

Tungsten is not readily forgeable. Sintered bars of tungsten are hot swaged rather than forged. However, sintered bars can be forged when heated to 3270°F. The temperature is reduced toward the end of the operation to 2000°F.

POWDER METALLURGY

The various physical, chemical, and mechanical properties of tungsten are such that the metal is generally produced by powder-metallurgy methods.

Tungsten metal powder is produced by the reduction of WO_3 by hydrogen. The particle size of the powder depends on the type and particle size of the oxide, impurities and additives present, temperature of reduction, time of reduction, and moisture content.

The tungsten powder is compacted in dies by use of a hydraulic press. Pressures of about 25 tons/sq in. are employed. After pressing, the fragile compacts are presintered at 1800 to 2200°F in hydrogen. This strengthens the compacts so that they can be handled easily and machined if necessary.

The presintered bars are given a final sinter in a hydrogen atmosphere. In this operation the bars are heated by passing a current through them. The maximum current used is about 95 percent of the current required for fusing the bar.

The sintered bars have a density of 16 to 18.5 gm/cm³ and can be ground and polished for certain uses. If a ductile metal is desired, the sintered bar is swaged or rolled.

JOINING

SOLDERING

Silver and soft solders are used to solder tungsten.

BRAZING

Tungsten can be brazed using copper, nickel, copper-nickel alloys, and probably other alloys. Conventional brazing equipment is suitable.

For high-temperature use, tantalum has been used as the brazing alloy.

WELDING

At present, welds in tungsten are likely to be brittle at room temperature. Oxidation is a problem in the welding of tungsten.

Spot welds are commonly made using a layer of nickel between the tungsten parts.

MACHINING

Abrasive wheels of silicon carbide are used to machine tungsten. Light pressure, high tool speed, and an abundance of coolant facilitate the grinding or cutting operations. Chipping and cracking can be avoided by careful operators.

Machining with hard-metal tools is possible.

HEAT TREATMENT

Tungsten can be stress relieved at temperatures of about 1830°F. The optimum annealing conditions depend on the history of the metal.

The fibrous structure of worked tungsten begins to change to an equiaxed structure when the metal is heated to about 1830°F or higher. However, various volatile and nonvolatile additives are commonly used to control the grain structure of tungsten.

RECRYSTALLIZATION AND GRAIN GROWTH

Commercial tungsten generally becomes brittle if the recrystallization temperature is exceeded to the extent that the grains of the metal are equiaxed. The recrystallization temperature of tungsten varies. It is established that, in general, the recrystallization temperature of tungsten is lowered markedly by the degree of cold working applied to the metal. The recrystallization temperature ranges from about 2820°F down to a dull red heat.

Additives to tungsten are used to restrict grain growth or to promote grain growth in certain directions of the wire products. The additions of alkaline oxides, silica, and boron volatilize from tungsten during sintering, facilitating the escape of the less volatile impurities in the metal. These volatile additives cause exaggerated grain growth. On the other hand, the nonvolatile additives, such as the oxides of thorium, uranium, and calcium, are grain-growth inhibitors. When both types of additives are used, tungsten can be produced which has exaggerated grain growth in one direction.

CORROSION BEHAVIOR

ATMOSPHERIC

Tungsten is not affected by air at room temperature when the metal is in other than powder form. Fine-powdered tungsten is pyrophoric.

At 750° to 930°F, tungsten begins to oxidize in air.

WATER

Tungsten resists water and water vapor at room temperature, but at red heat the metal is oxidized rapidly to WO_3 and blue oxide.

LIQUID METAL

Tungsten has good corrosion resistance (rate of attack less than 1 mil/yr) in the following molten metals: mercury (570° and 1110°F), sodium (570° and 1110°F), potassium (570° and 1110°F), gallium (570° and 1110°F), and magnesium (1200°F). At 1800°F, tungsten is reported to have disintegrated in molten lithium contained in Armco iron.

OTHER

Alkali solutions and ammonia do not corrode tungsten in the absence of oxygen. Tungsten is not attacked by hydrofluoric acid. Hot concentrated nitric acid dissolves the metal slowly, but hot concentrated hydrochloric acid and hot concentrated sulfuric acid react only slightly with the metal.

Solutions of $CuCl_2$ or $FeCl_3$ corrode tungsten. Tungsten anodes in caustic solutions are dissolved rapidly.

Fluorine attacks tungsten at room temperature, and bromine and iodine attack the metal at red heat. The gases CO_2 , CS_2 , S_2Cl_2 , CO , NO , and NO_2 react with tungsten at high temperatures. Carbon, boron, silicon, and sulfur form compounds with tungsten at high temperatures. Tungsten reacts with MgO , Al_2O_3 , ThO_2 , and ZrO_2 at very high temperatures.

Molten nitrates, nitrites, and peroxides react violently with tungsten. Tungsten resists molten sodium or potassium hydroxides but the presence of KNO_3 , KNO_2 , $KClO_3$, PbO_2 , or other oxidants in these hydroxides will cause corrosion of tungsten at a high rate.

METALLOGRAPHY

Conventional methods can be used to mount and polish tungsten specimens. Etching agents commonly used include:

- | | |
|--|--|
| 1. 5 gm of NaOH
15 gm of $K_3Fe(CN)_6$
100 cm ³ of H_2O | Use cold; etch for 10 sec |
| 2. 5 gm of NaOH
30 gm of $K_3Fe(CN)_6$
100 cm ³ of H_2O | Produces etch pits in single crystals |
| 3. 35 cm ³ of HF
15 cm ³ of HNO_3
50 cm ³ of H_2O | Use hot; produces etch pits |
| 4. 40 gm of NaOH
20 cm ³ of H_2O_2
100 cm ³ of H_2O | Electrolytic etchant; suitable current density and voltage must be determined for each particular specimen |

Small tungsten specimens are often mounted in a low-melting-point glass.

ALLOYS OF TUNGSTEN

The alloys of tungsten can be classified in three groups:

1. Ferrous alloys containing tungsten.
2. Tungsten carbide.
3. Nonferrous alloys containing tungsten.

Innumerable ferrous alloys in wide usage contain up to 20 percent tungsten as an addition. The tungsten enables the steel to resist the effects of high temperature and forms hard, wear-resistant carbides in the steel. The high-speed steels (18 percent W) are the most widely used tungsten-containing steels. Hot-work steels (10 percent W) are used in operations where a minimum loss of hardening is desired when the steel is used at about the tempering temperature. Finishing steels (3.5 percent W) maintain a keen cutting edge. Tungsten is added to other steels for various reasons, e.g., creep resistance, high strength at elevated temperatures, and high density.

The properties of tungsten carbide make it a unique material. Because of its high hardness and transverse strength, tungsten carbide is a component of hard materials used for dies, tools, and wear-resistant parts. Various materials containing tungsten carbide are available. The materials are generally brittle, a property that is undesirable in many applications.

Nonferrous alloys containing tungsten include the Stellites which are corrosion and wear resistant. Tungsten, bonded with copper and nickel in a powder-metallurgy process, is a useful material in that densities of more than 17 gm/cm³ can be obtained.

CONSTITUTIONAL DIAGRAMS

The principal constitutional diagrams of tungsten include carbon-, cobalt-, iron-, molybdenum-, nickel-, and carbon-iron-tungsten. The recent versions of these diagrams are available in the ASM "Metals Handbook," 1948 edition. The tungsten-uranium constitutional diagram is shown in Chap. 1.22 of this section.

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CHAPTER 1.22

Uranium and Its Alloys

H. A. Saller

REACTOR APPLICATION

Uranium is the basic fuel material for reactors. Any reactor must contain either one of the fissionable isotopes of uranium or plutonium, which is itself made from uranium.

In the earliest and simplest reactors, natural uranium, containing about 0.7 percent of the fissionable isotope U-235, was used as a fuel in the form of massive-metal slugs. By employing sufficient quantities of fuel and a suitable moderator, such reactors are self-sustaining and produce plutonium.

Most of the reactors now operating use uranium in the form of pure massive-metal slugs. Reactors designed to operate at high flux or high temperatures use uranium enriched in U-235 and diluted by alloying with some low-cross-section metal, such as aluminum or zirconium. Such reactors may be used to produce power.

In other reactors, uranium may be incorporated in low-melting, metal eutectics or as a part of a molten salt. It may also be used as oxide or carbide embedded in metal, graphite, or suitable ceramic material.

ABUNDANCE AND AVAILABILITY

Prior to the Manhattan Project, metallic uranium was a laboratory curiosity. Some uranium ores were mined in the Belgian Congo or at Great Bear Lake in Canada, primarily to obtain the radium which occurred with it. Similarly, deposits in Colorado were worked to obtain vanadium. Some uranium oxide was produced as a coloring material for the ceramic industry.

While uranium has been considered extremely rare, it does make up 0.0004 percent of the earth's crust, considerably more than such metals as cadmium, bismuth, mercury, and silver which are not considered unusually rare. Uranium is found in various types of rock as a great variety of minerals. The highest concentrations occur in igneous rocks; sedimentary rocks (sandstones) contain much less, perhaps only half as much. Uranium has been found in sea water, river water, and in living organisms.

From the viewpoint of richness of deposit, pitchblende is the most important uranium mineral. Its composition varies but approaches UO_2 in the unweathered condition. The uranium found at both Great Bear Lake and the Belgian Congo occurs as pitchblende or one of its oxidation products.

The principal uranium-bearing deposits in the United States are found in Colorado and Utah where the uranium occurs as carnotite and roscoelite. These minerals are made up primarily of silica as sand grains with a matrix of fine clay-like materials containing the uranium ores and usually vanadium as vanadyl vanadates, calcium vanadates, or vanadium micas. The uranium content of these ores is generally low averaging about 0.2 percent U_3O_8 .

Uranium also occurs as columbates, tantalates, titanates, phosphates, silicates, carbonates, sulfates, and arsenates, but their minerals generally are not of commercial importance as sources of uranium. A plant is being built, however, to recover U_3O_8 from phosphates.

EXTRACTION AND PURIFICATION

Two processes are used to extract uranium from its ores: one for pitchblendes, the other for carnotites. There are, of course, many minor variations of each.

The two principal types of pitchblende are Canadian, which contains commercial amounts of gold and silver, and African, which contains very little. Canadian pitchblende is treated by a variety of mechanical and chemical processes. In one method¹ the pulverized ore is first concentrated by mechanical separation and flotation, and the uranium-bearing product from flotation ordinarily is treated to recover the gold and silver (for example, by cyanidization or a controlled salt roast and leach). The uranium-bearing material is subsequently leached with sulfuric acid, and after chemical purification, the uranium is precipitated as ammonium diuranate which is then ignited to form U_3O_8 .

African pitchblende is concentrated by gravity. The concentrate is U_3O_8 of such purity that it can go directly to the solvent-extraction purification process described later. The middlings are dissolved in acid and treated with magnesium hydroxide. The uranium-bearing precipitate can be fed into the purification process in controlled quantities along with the pitchblende concentrates.

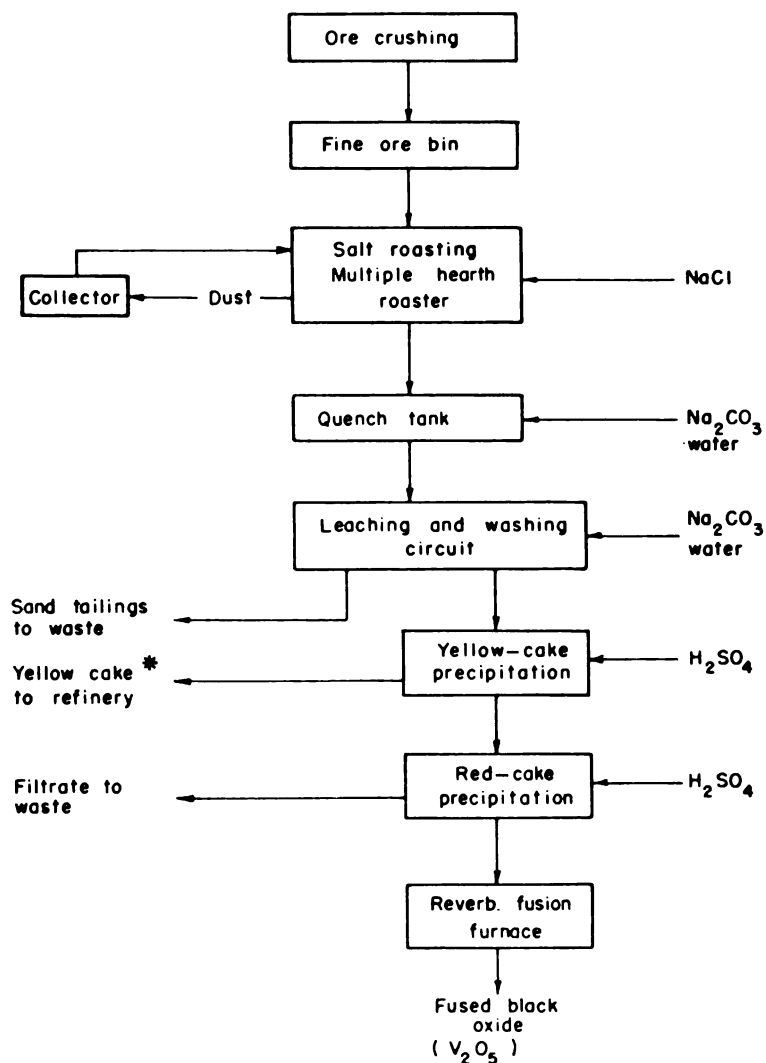
Carnotite ores, such as those found in western United States, are treated by one of four methods, depending largely on the amount of vanadium in the ore and whether it is desirable to recover it. Prior to 1940, a considerable tonnage of carnotite ores was processed principally for the vanadium, while the uranium-bearing portion was stored as tailings.

The four concentration processes for carnotites are: (1) salt roast-carbonate leach, (2) salt roast-acid leach, (3) no roast-carbonate leach, and (4) no roast-acid leach. The first two are quite old and generally are used where it is desirable to recover the vanadium portion of the ores. Figure 1.22.1 is a flowsheet of the salt roast-carbonate leach process. The flowsheet for the salt roast-acid leach process is shown in Fig. 1.22.2.

Low-vanadium carnotites are treated either by direct acid leaching or by the carbonate process. For direct acid leaching, the ground ore is treated with acid, usually H_2SO_4 . The uranium is won from the acid solution by various methods including precipitation by pH control. The two variations of the carbonate process are described in the simplified flow sheets of Fig. 1.22.3. Final products are further refined to produce high-purity uranium trioxide.

Uranium metal can be prepared by several methods. In 1789, Klaproth reduced UO_3 with carbon, obtaining what was then considered to be uranium metal. Peligot showed, in 1840, that Klaproth's product was UO_2 and succeeded in preparing the metal by the reduction of UCl_4 with potassium. Following Peligot's work, a number of investigators produced small quantities of uranium metal powder on a laboratory scale by four methods: (1) Reduction of uranium oxide with carbon, (2) reduction of uranium oxides with aluminum, calcium, or

¹References appear at end of chapter.



* In refinery, the yellow cake (a uranyl vanadate) is fused with Na_2CO_3 and sawdust to form UO_2 and a water soluble sodium vanadate which is recycled to the red cake precipitation

Fig. 1.22.1 — Simplified Flowsheet of the Carbonate Process for Concentrating Carnotites. Reprinted from V. L. Saine and K. B. Brown, Studies of Recovery Processes for Western Uranium-Bearing Ores, Y-499, Oct. 14, 1949.

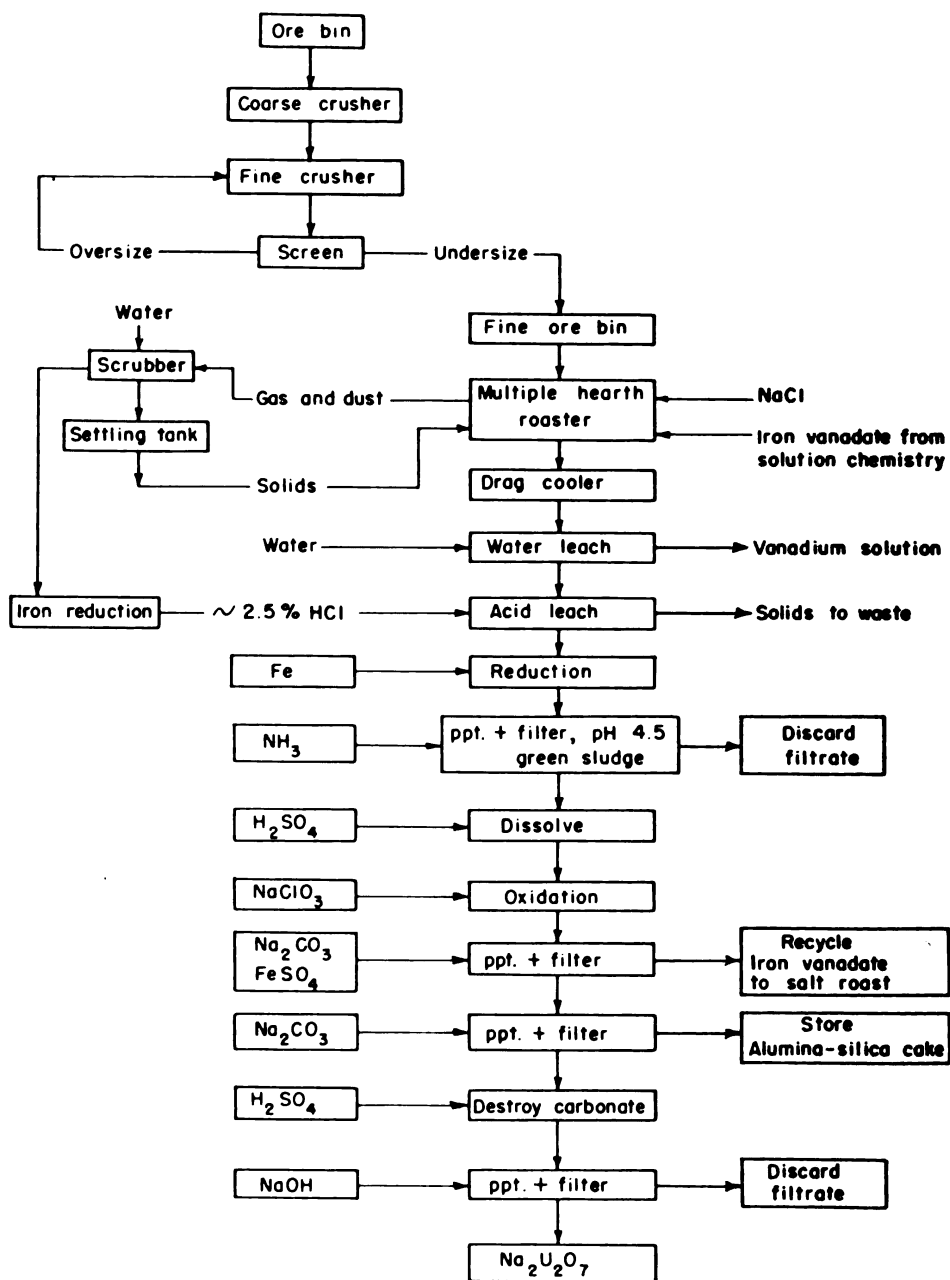


Fig. 1.22.2 — The Simplified Flow Sheet for the Salt Roast-acid Leach Concentration Process. Reprinted from V. L. Saine and K. B. Brown, *Studies of Recovery Processes for Western Uranium-Bearing Ores*, Y-499. Oct. 14, 1949.

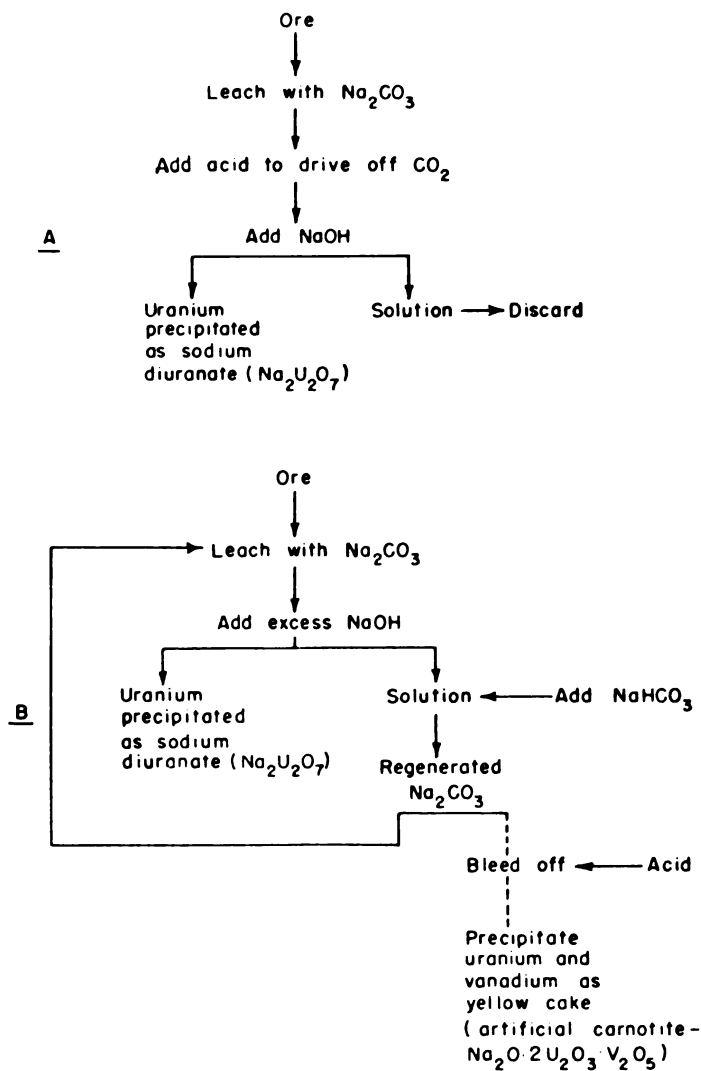


Fig. 1.22.3 — The Two Variations of the Carbonate Process for Low-vanadium Carnotites. Reprinted from V. L. Saine and K. B. Brown, *Studies of Recovery Processes for Western Uranium-Bearing Ores*, Y-499, Oct. 14, 1949.

magnesium, (3) reduction of uranium halides with alkali metals or alkaline-earth metals, and (4) electrolysis of uranium halides.

At the time the MED Project was started, uranium was being produced by two methods in the United States. Metal Hydrides, Inc. was making pure uranium powder by reacting uranium dioxide with calcium hydride, and Westinghouse had produced metal powder by the electrolysis of potassium-uranium fluoride, KUF_5 , dissolved in a bath of fused alkali and alkaline-earth chlorides. Small amounts of the metal had been melted, cast, and drawn into wire. Both production methods were expanded considerably, and techniques were developed for melting and casting the powder or sintered blocks produced. The high cost and low yields of both production methods, however, led to the development on a commercial scale of the bomb-reduction process described below.

Spedding and his associates at Iowa State College² in 1942 studied the production of metallic uranium from its oxides or halides by reacting them with calcium, magnesium, aluminum, sodium, or carbon. This research led to the present commercial bomb-reduction process.

For some applications requiring special purity, metallic uranium is produced by the electrolysis of various uranium halides. Uranium powder of a high degree of purity is produced rather easily by treating uranium metal with hydrogen at around 450°F to form the hydride. This hydride is then decomposed by heating in vacuum at about 900°F.

PHYSICAL AND CHEMICAL CONSTANTS

Various values for physical and chemical constants of uranium are listed in the literature. Early work is subject to error owing to the relatively impure metal available. For example, constants determined on the MED Project reflect the changes in the quality of metal as new and better refining methods were introduced. The values reported in this chapter are selected as the best available at the present time. The principal physical and chemical constants of uranium are listed in Table 1.22.1.

Table 1.22.1 — Physical and Chemical Constants of Uranium

Density, * gm/cm ³	
Theoretical, from X-ray data	19.13
Wrought material	18.5–19.0
Pressed and sintered powder	18.9
Melting point, °C	1133 ± 1
Boiling point, °C	3900
Heat of fusion, kcal/mole	2.5–3.0
Heat of vaporization, kcal/mole	93
Specific heat, † cal/(mole)(°C)	
–249.28°C	1.211
–201.61°C	4.657
–149.70°C	5.639
–99.57°C	6.053
–0.16°C	6.524
27°C	6.649
227°C	7.606
427°C	8.952
627°C	11.107
774 (β) °C	10.147
774 (γ) °C	9.177
827°C	9.147

Table 1.22.1 — (Continued)

Enthalpy (H_T), cal/mole			
27°C			1,539
127°C			2,202
227°C			2,935
327°C			3,725
427°C			4,583
527°C			5,520
627°C			6,567
727°C			8,337
827°C			10,430
Entropy, cal/(mole)(°C)			
27°C			12.052
127°C			13.941
227°C			15.601
327°C			17.058
427°C			18.387
527°C			19.646
627°C			20.882
727°C			22.760
827°C			24.761
Electrical resistivity, μohm-cm			
25°C			$2-4 \times 10^4$
Thermal conductivity, $\frac{\text{cal}}{(\text{sec})(\text{cm})(^\circ\text{C})}$			
Thermal expansion, 10^{-6} per °C			
From X-ray data,			
direction parallel			
to axis	25°–125°C	25°–325°C	25°–650°C
(100)*	21.7	26.5	36.7
(010)†	–1.5	–2.4	–9.3
(001)‡	23.2	23.9	34.2
Volume	45.8	48.6	61.5
[100] $l_t = 127^\circ (1 + 17.2 \times 10^{-4}t + 30.8 \times 10^{-6}t^2)$			
[010] $l_t = 127^\circ (1 - 9.2 \times 10^{-4}t + 40.4 \times 10^{-6}t^2 - 67.5 \times 10^{-12}t^3)$			
[001] $l_t = 127^\circ (1 + 25.1 \times 10^{-4}t - 21.3 \times 10^{-6}t^2 + 57.5 \times 10^{-12}t^3)$			
Volume $V_t = V_{27^\circ} (1 + 45.0 \times 10^{-4}t - 3.4 \times 10^{-6}t^2 + 5.0 \times 10^{-12}t^3)$			
Allotropic transformations, °C			
Type of material	Heating		Cooling
	$\alpha-\beta$	$\beta-\gamma$	$\gamma-\beta$ $\beta-\alpha$
High-purity	663	764	762 660
electrolytic			
Bomb-reduced	661	763	761 652

*Gm/cm³ \times 62.43 = lb/cu ft†Cal/(mole)(°C) \times 1 = Btu/(lb mole)(°F)

‡See Fig. 1.22.4

§Cal/(sec)(cm)(°C) \times (2.419 \times 10²) = Btu/(hr)(ft)(°F)

¶See Fig. 1.22.5

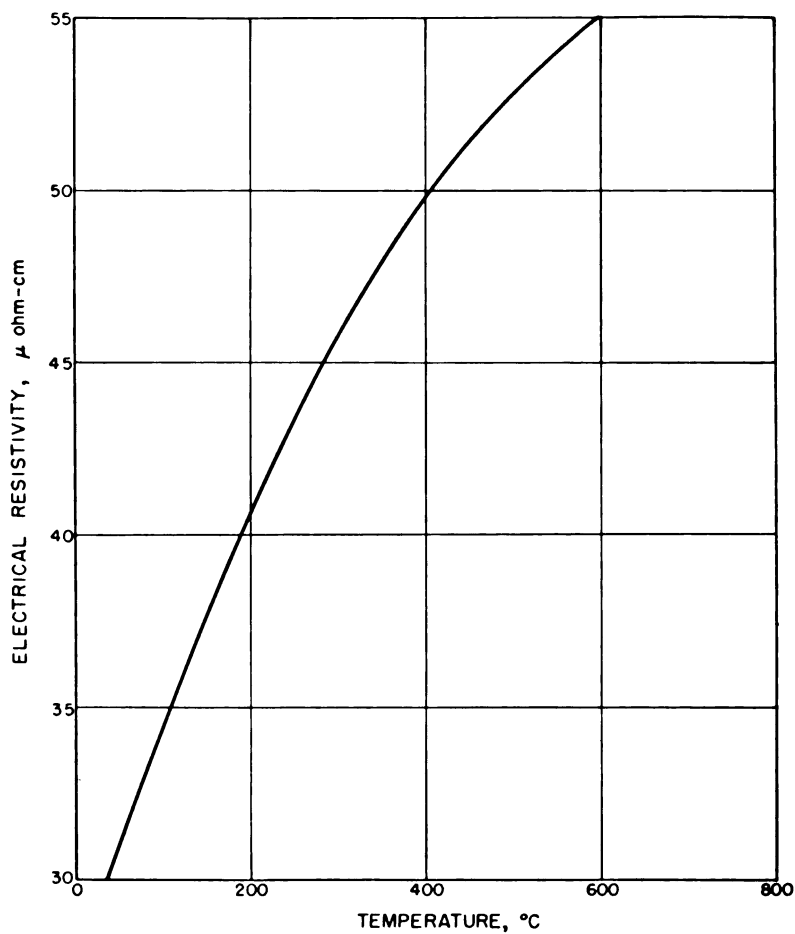


Fig. 1.22.4—The Electrical Resistivity of Uranium Versus Temperature.
Submitted by Battelle Memorial Institute, Oct. 1, 1952.

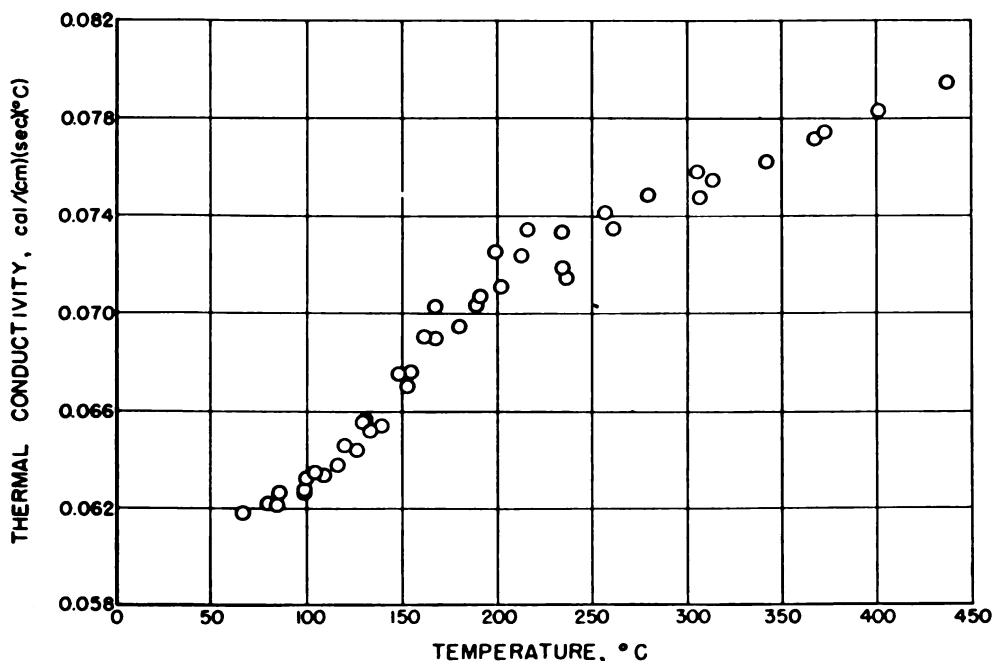


Fig. 1.22.5 — The Thermal Conductivity of Uranium at Various Temperatures. Reprinted from Joseph J. Katz and Eugene Rabinowitch, *The Chemistry of Uranium*, NNES, Division VIII, Vol 5, Chapter 4, McGraw-Hill, 1951.

CRYSTALLOGRAPHY

Uranium metal exhibits three crystalline forms. The alpha phase is stable up to 660°C. It crystallizes in the orthorhombic system with space group D_{2h}^{17} . The unit-cell dimensions are $a_0 = 2.854$ Å, $b_0 = 5.867$ Å, and $c_0 = 4.957$ Å. Its structure may be regarded as stacks of corrugated sheets of atoms with interatomic distances of 2.8 Å and 3.3 Å. Binding within the sheets is largely covalent, forming a layer structure analogous to that of arsenic, antimony, and bismuth. Figure 1.22.6 shows the variation of lattice constants with temperature.

The beta phase exists between 660° and 760°C. Its crystal structure is tetragonal with $a_0 = b_0 = 10.590$ Å and $c_0 = 5.634$ Å. Each cell contains 30 atoms.

Gamma uranium exists from 760°C up to the melting point. It has a body-centered cubic structure with $a_0 = 3.474$ Å.

Uranium deforms both by twinning and by slip. Twinning is important only below about 350°C. The predominant twinning plane is (130), but there is evidence that other twins occur to a lesser degree. According to Cahn of AERE, the principal slip system is (010) [100] and, less prevalent, (110) with the slip direction probably $[1\bar{1}0]$.

According to Turkalo, Burke, and Holden, the (001) plane is approximately parallel to the rod axis following all working conditions. There is a spread of ± 30 degrees which is independent of temperature. The plane which is parallel to the cross section of the bar changes with changes in working temperatures. At the higher working temperatures, 500° and 600°C, a mixed texture is found with planes (010) and (110) both lying perpendicular to the rod axis, although the (110) texture predominates. At lower working temperatures, the population of (010) planes increases while the population of (110) planes decreases until at temperatures below 300°C the (110) planes are randomly oriented and only the (010) texture is present. The increased incidence of (010) texture at low deformation temperature

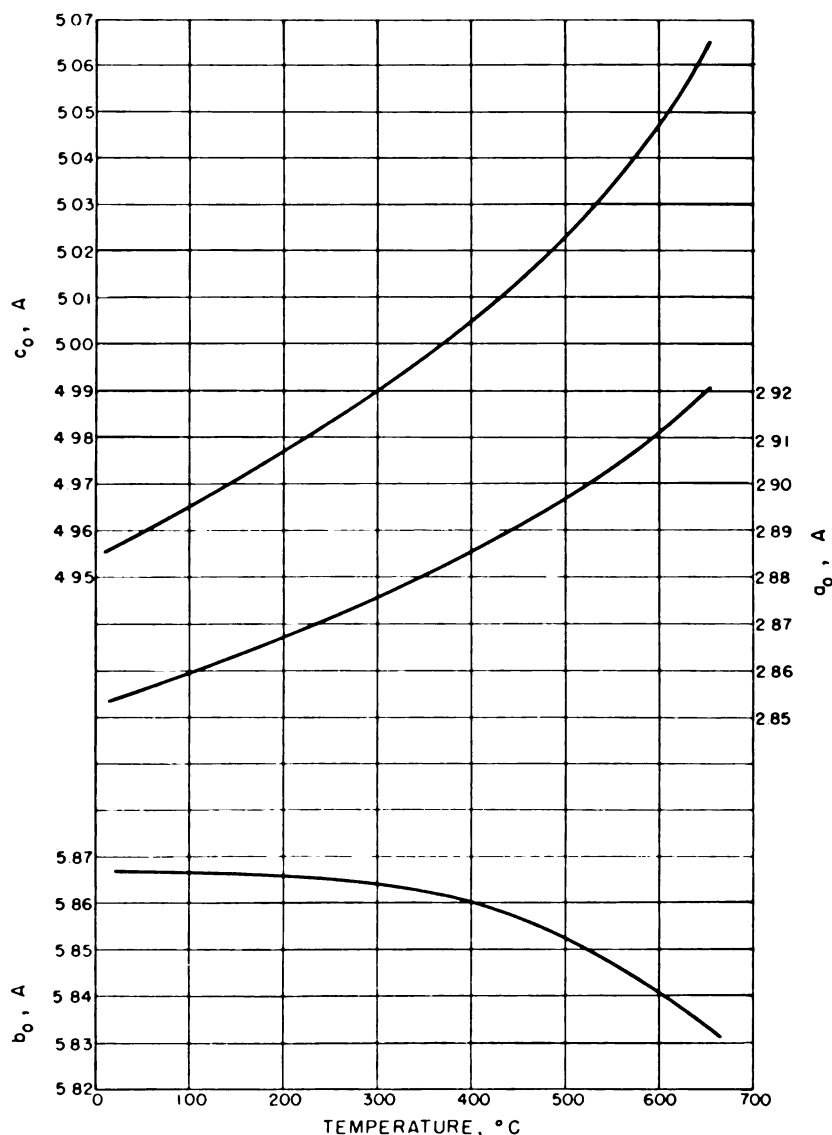


Fig. 1.22.6 — The Unit-cell Dimensions of Alpha Uranium as a Function of Temperature. Submitted by Battelle Memorial Institute, July 1, 1952.

is explained by KAPL by means of a (130) twinning mechanism, whereby (110) planes are transformed into (010) planes perpendicular to the rolling direction.

Fisher of Argonne reports that the 300°C rolling texture of uranium was found to be a duplex fiber structure with the (010) plane perpendicular to the rolling direction in the major texture component and the (110) plane perpendicular to the rolling direction in the minor texture component. The (001) plane was parallel to the rolling direction in both components.

The recrystallization texture was a duplex fiber texture consisting of the retained (010) rolling component and a new component which corresponded to a rotation of about 30° to 35° of the (110) component about the "c" axis. The (001) plane remained parallel to the rolling direction.

HEALTH HAZARDS

Uranium constitutes a health hazard both from whole-body radiation and inhalation of its dusts. Competent advice on this problem can be obtained from the health-physics groups of the various laboratories and the Atomic Energy Commission.

HANDLING AND STORAGE

Massive uranium metal offers no real problem in handling and storage. The surface oxidizes slowly in contact with air; the oxide is adherent and, once formed, tends to prevent any further reaction. Finely divided uranium metal, however, such as chips, powder, and the like, is quite pyrophoric. Care must be exercised during handling and storage to prevent serious fires and explosions. Fine uranium scrap can be safely stored by first burning it to form the oxide. This should be done in small batches with the workers protected by face shields and respirators. Uranium metal should be handled wet or in an inert atmosphere. Dry boxes are recommended for most laboratory manipulations.

Uranium has been stored in mineral oil, CCl_4 , and other organic liquids. Uranium to be stored under these agents should first be cleaned and dried. Uranium can also be stored under water if extreme care is taken to see that all the metal is immersed and that the hydrogen which is evolved is removed by proper ventilation.

MECHANICAL PROPERTIES

The mechanical properties of uranium are affected considerably by orientation, which in turn is controlled by fabricating history and heat treatment. Minor variations in the carbon content also have a marked effect on mechanical properties. The figures reported below represent either a good average value or are used to show the variation of properties under certain conditions. The effect of alloying elements is discussed later under "Uranium Alloys."

TENSILE PROPERTIES

Tensile properties of uranium under various conditions of fabrication, heat treatment, and carbon content are shown in Tables 1.22.2 through 1.22.5.

Accurate values of Poisson's ratio and the elastic modulus have been very difficult to obtain because of the low proportional limit (2000-4000 lb/sq in.) of uranium. To get reasonable values from the straight-line portion of the stress-strain curve, elongations must be measured within accuracy limits not yet obtainable.

Values of Young's modulus, shear modulus, and Poisson's ratio, determined by dynamic means based on the measurements of sound velocities, are given in Table 1.22.6.

COMPRESSION DATA

Compression data are given in Table 1.22.7 and Fig. 1.22.7.

HARDNESS

The hardness of alpha-rolled uranium is given in Table 1.22.8, and the hardness of alpha- and gamma-extruded uranium is shown in Fig. 1.22.8.

IMPACT STRENGTH

The impact strength of uranium at various temperatures is given in Table 1.22.9.

SHEAR STRENGTH

Table 1.22.10 gives data on the shear strength of uranium having various fabrication histories.

CREEP

Typical creep values of uranium are given in Table 1.22.11.

WORK-HARDENING CHARACTERISTICS

Figure 1.22.9 is a comparison of the work-hardening rates of uranium, 18-8 steel, nickel, and aluminum.

Table 1.22.2 — Tensile Properties of Uranium Extruded at Various Temperatures

Extrusion Temp., °F	Ratio	Yield strength (0.1% offset), 10 ³ lb/sq in.	Tensile strength, 10 ³ lb/sq in.	Reduction in area, %	Elongation, %	Young's modulus, 10 ⁶ lb/sq in.
390	2-1	52	127	7	6	22
750	2-1	46	125	13	11	24
750	8-1	32	103	18	18	18
930*	8-1	28	96	2	13	16
1110	14-1	28	96	15	20	16

*Metal was high in impurities

Table 1.22.3 — Tensile Properties of Uranium at Elevated Temperatures

Specimen*	Test temperature, °F	Yield strength (0.2% offset), lb/sq in.	Ultimate strength, lb/sq in.	Elongation, %
570°F rolled				
Alpha annealed†	Room	43,300	111,100	6.8
Beta annealed‡	Room	24,550	63,800	8.5
1110°F rolled				
Alpha annealed	Room	26,000	88,400	13.5
Beta annealed	Room	24,600	61,700	6.0
570°F rolled				
Alpha annealed	570	17,500	35,200	49.0
1110°F rolled				
Alpha annealed	570	18,800	31,570	43.0
Beta annealed	570	15,300	26,900	33.0
570°F rolled				
Alpha annealed	930	5,100	11,130	61.0
Beta annealed	930	7,100	10,500	44.0
1110°F rolled				
Alpha annealed	930	5,450	10,450	57.0

*All specimens were standard 0.505-in. rounds

†Alpha anneal is 12 hr at 1110°F, slow cooled

‡Beta anneal is 12 hr at 1290°F, slow cooled

Table 1.22.4—Low-temperature Tensile Properties of Uranium* in Various States of Heat Treatment

Heat Treatment	Test temp., °F	Yield strength (0.2% offset), 10 ³ lb/sq in.	Ultimate strength, 10 ³ lb/sq in.	Reduction in area, %	Elongation in 2 in., %	Modulus of elasticity, 10 ⁶ lb/sq in.	Poisson's ratio
As cast	75	28	56	10	4	24	0.21
	-50	28	47	4	3	26	...
	-100	27	42	3	3	26	...
As alpha rolled (1020°F)	75	31	96	10	11	25	0.22
	-50	40	109	4	4	24	...
	-100	37	87	4	3	23	...
Alpha rolled and gamma annealed (1560°F)	75	26	57	10	5	21	0.18
	-50	27	43	4	3	31	...
	-100	17	36	5	3	26
Alpha rolled and beta quenched (1335°F)	75	36	84	12	9	24	0.24
	-50	40	92	6	5	27	...
	-100	42	88	5	4	30	...
Alpha rolled, beta quenched (1335°F) and alpha annealed (1020°F)	75	32	90	12	12	22	0.19
	-50	33	83	5	5	31	...
	-100	37	89	6	6	27	...

*All specimens were standard 0.505-in. rounds

Table 1.22.5 — The Effect of Carbon Content on the Tensile Properties of Uranium*

Carbon content, ppm	Total impurities, ppm	Yield strength, (0.2% offset), 10 ³ lb/sq in.	Ultimate strength, 10 ³ lb/sq in.	Elongation in 2 in., %	Modulus, 10 ⁶ lb/sq in.
60	260	20	52	8	23
210	410	22	53	8	24
360	525	28	59	8	23
550	650	29	72	11	25
630	815	28	75	17	24
710	1,000	28	70	12	23
820	925	25	62	9	30
1,250	1,800	25	74	10	24

*All specimens cut from cast plates and pulled in as-cast condition; specimens were standard 0.505-in. rounds

Table 1.22.6 — Young's Modulus, Shear Modulus and Poisson's Ratio for Uranium in Various Conditions of Fabrication

Condition	Young's modulus, 10 ⁶ lb/sq in.	Shear modulus, 10 ⁶ lb/sq in.	Poisson's ratio
Swaged and annealed	29.1	11.9	0.22
Gamma extruded	29.3	12.0	.21
Gamma extruded	30.3	12.1	.25
Cast	29.5	12.1	.22
Cast	30.0	12.1	.24
Average	29.7	12.1	.23

Table 1.22.7 — Compression Tests on Uranium

Material	Test temp., °F	Yield strength (0.5% offset), 10 ³ lb/sq in.	Deformation at proportional limit, in.	Deformation at yield strength, in.	Deformation at 120,000 lb/sq in., in.	Modulus, 10 ⁶ lb/sq in.
As-cast (500 ppm carbon 700 ppm total impurities)	-5	85	0.016	0.080	0.174	2.6
	75	111	.044	.070	.083	5.3
	300	86	.034	.080	.153	3.0
	390	81	.017	.084	.176	2.2
	480	60	.018	.086	.290	1.7
	570	48	.022	.092	.364	1.2
Alpha-rolled (600 ppm carbon 1000 ppm total impurities)	-5	90	0.036	0.133	0.205	1.1
	300	87	.034	.081	.142	3.0
	390	63	.013	.077	.205	2.2
	480	67	.018	.089	.264	1.7
	570	42	.023	.110	.427	0.7

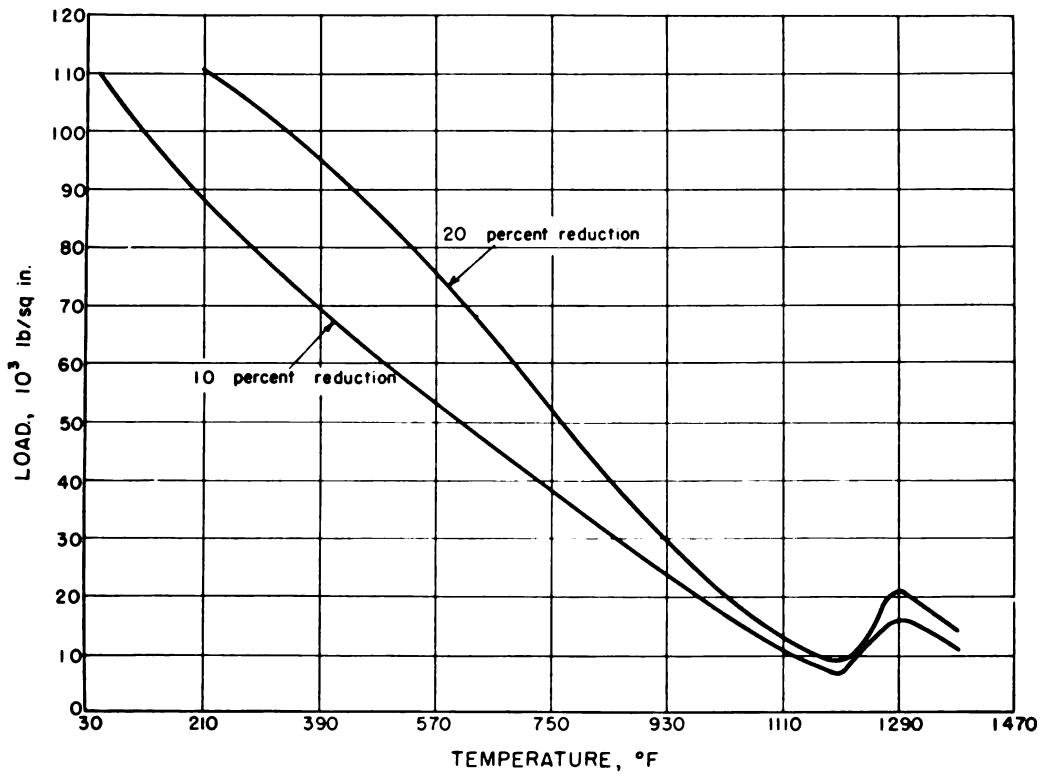


Fig. 1.22.7 — The Compression Pressure Versus Temperature Relationship for Uranium. Reprinted from A. N. Holden, A Note on the Ductility of Beta Uranium, KAPL-408, Sept. 28, 1950.

Table 1.22.8 — Hardness of α -Rolled Uranium*

Scale	Transverse specimen	Longitudinal specimen
Rockwell B	97	98
Rockwell G	80.5	83
Vickers diamond (10- to 15-kg load)	220	240
Vickers diamond (30- to 45-kg load)	...	250
Brinell (calculated from R_B)	240	260
Brinell (calculated from R_G)	250	280
Knoop (200-gm load)	280	320
Knoop (500-gm load)	250	300
Knoop (1000-gm load)	240	320
Eberbach (263-gm load)	270	300
Eberbach (645.6-gm load)	260	290

*All readings taken on the same sample

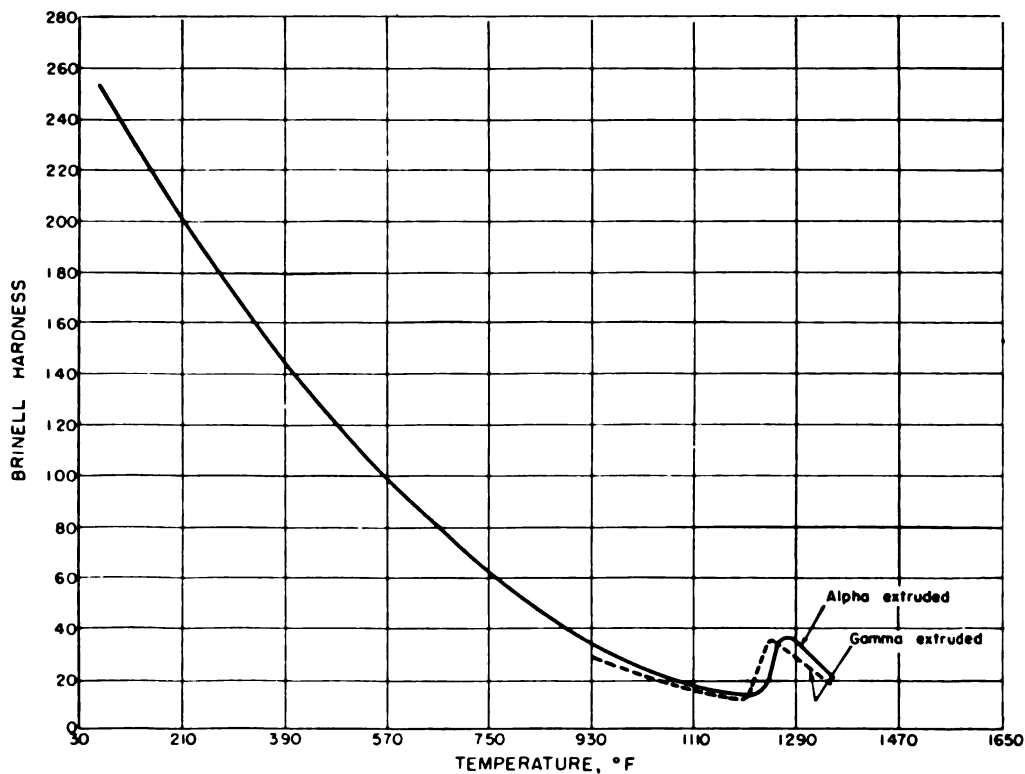


Fig. 1.22.8 — The Hardness of Uranium at Various Temperatures. Reprinted from A. N. Holden, A Note on the Ductility of Beta Uranium, KAPL-408, Sept. 28, 1950.

Table 1.22.9 — Impact Strength of Uranium*

Temperature, °F	Laboratory B						
	Laboratory A						
	Alpha rolled†	Forged‡	Alpha rolled§	As cast§	Beta quenched§	Beta quenched, alpha annealed§	Gamma annealed§
-290	5	4
-100	6	8	5	6	8
-75	8	10	6	7	8
-50	10	12	7	7	10
-25	10	12	7	8	11
0	12	12	8	9	13
50	14	13	9	10	16
75	11	6	14	14	11	12	16
100	15	15	12	14	17
150	18	17	15	20	22
200	25	23	18	27	28
300	27	11	32	27	29	52	50
390	...	18
480	57	36
570	76	70
610	...	85
615	85
645	...	102
750	109

*All samples standard V-notch Charpys. Values given in ft/lb

†Normal material: 600 ppm carbon, 1000 ppm total impurities

‡High-purity material: 240 ppm carbon, 333 ppm total impurities

§Normal purity

Table 1.22.10 — The Shear Strength of Uranium*

Condition†	Shear Strength, 10 ³ lb/sq in.		
	½ in. diam.	¼ in. diam.	⅜ in. diam.
As cast	85	84	75
Cold swaged‡	127	114	95
Cold swaged as above and annealed at 1100°F	83	88	80
Rolled at 1110°F	80	79	77
Rolled 62-½% at 1110°F and rolled 68% at 615°F	113	95	...
Rolled as above and annealed at 1110°F	83	88	81

*430 ppm carbon, 613 ppm total impurities

†All samples tested at room temperature

‡½-in. specimen, 94%; ¼-in. specimen, 75%; ⅜-in. specimen, 44%

Table 1.22.11 — Creep of Uranium at 930°F

Annealing history*	Stress, lb/sq in.	Time, hr	Total deformation, %	Minimum secondary creep rate, %/hr	Grain size after test, mm
10 hr at 1290°F	2750	1530	3.72	0.0025	...
and 10 hr at 1110°F	2220	1200	2.20	.0013	0.12–0.13
	1720	1700	0.82	.0003	.10–.11
	1500	1515	.85	.00035	...
10 hr at 1110°F	2220	1200	4.72	0.0018	0.045–0.05
	1720	1350	1.92	.0009	.05–.055

*All specimens 1110°F rolled

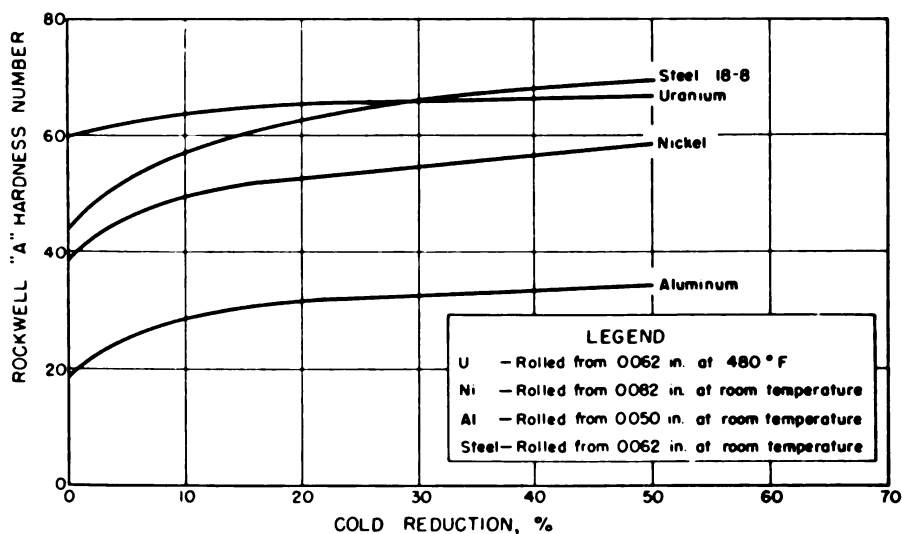


Fig. 1.22.9— The Relative Work-hardening Rates of Uranium, 18-8 Stainless Steel, Nickel, and Aluminum. Reprinted from W. C. Gribble, et al., Deep Drawing of Uranium, LA-1150, Dec. 15, 1950.

FATIGUE

The fatigue strength of alpha-extruded uranium was measured on a Krouse 10,000 rev/min cantilever-beam machine. At 35,000 lb/sq in., specimens failed after 1.2×10^5 to 2.5×10^6 cycles.

MELTING AND CASTING

It is necessary that uranium be melted and cast into some shape suitable for further fabrication. Melting and casting are extremely difficult by the high degree of chemical reactivity of uranium with the atmosphere and with most crucible materials. The first problem has been solved by melting in vacuum in an inert atmosphere or under a suitable slag or flux. The second problem has been partially solved with some sacrifice of metal purity. Both problems continue to receive attention.

FORMING AND FABRICATION

When large quantities of uranium metal became available to the Manhattan Project, it was necessary to devise means of fabricating these ingots into various shapes. Early efforts were concentrated on extrusion and rolling, and both methods were developed to a high state of efficiency. More recently, other methods of fabrication including forging, pressing, swaging, and drawing have been investigated and workable techniques established.

The ease of fabrication of uranium varies greatly with temperature. In the gamma phase, uranium is so soft and plastic that rolling and swaging are difficult. The beta phase is generally harder and more brittle than the other two phases, but with close temperature control, some rolling and extrusion have been accomplished in the beta region. Most of the fabrication, however, is done in the alpha phase; some care must be exercised to prevent oxidation, but generally the metal is quite easy to fabricate.

EXTRUSION

While the first work on extrusion indicated it could be done in either the alpha or the gamma phase, the pressures required in the alpha phase were high. For gamma extrusion, the uranium slugs were heated to 1700°F in a reducing atmosphere and extruded by the direct method. Extrusion liners and dies wore rapidly, but use of refractory alloys of the "Stoodite" type overcame this trouble. For alpha extrusion the uranium can be either copper plated or handled bare. A soft-steel cone is placed in front of the uranium, and graphite "cutoff" cylinders are charged after the uranium.

Impact extrusion in the gamma phase (1920°F) has been used successfully to form a number of shapes, and it appears feasible to form any number of complicated shapes by this process. Extruded shapes have much better physical properties than similar cast shapes.

DRAWING

Uranium wire and tubing have been cold drawn with considerable success. For any drawing, the lubricant is the most critical factor. Tubing was drawn by the Superior Tubing Company using one of their proprietary lubricants. Rods and wire have been drawn using the following lubricant developed primarily for thorium: 100 cm³ of Duco black lacquer, No. 246-2048 (thinned 3 to 1 with lacquer thinner), mixed with 30 gm of Molykote (molybdenum disulfide), and 10 gm of fumed lead-zinc oxide. The lubricant is sprayed or brushed on and allowed to dry before drawing. It may be necessary to recoat the wire

after two or three drawing passes. Reductions of 20 percent per pass are feasible with this lubricant.

Wire has been drawn down to 0.003 in. in diameter by silver plating the wire prior to drawing. Some success has been achieved with copper plated wire.

ROLLING

While uranium can be rolled in the beta and gamma phase with some difficulty, most of it is processed in the alpha. Rolling is done in the range from room temperature to 1110°F. Uranium has been rolled using rolls of many shapes including diamonds, squares, guide rounds, hand rounds, ovals, and gothics. Uranium rolls easily and large reductions per pass may be taken.

A number of methods have been employed to heat uranium for rolling. These include inert-atmosphere furnaces, oil baths, lead baths, and salt baths.

Thin uranium foil of very good quality down to 0.0005 in. thick has been produced by cold rolling. In one method, starting stock 0.020 in. thick is produced by hot rolling. This is then cold rolled on a "four-high" mill with 1-in. work rolls. A large number of passes and about two anneals are required during the rolling. Recently, 2-mil foil has been rolled directly from 20-mil stock with no anneals by using a Sendzimer Mill.

FORGING

Uranium has been forged successfully at 930° to 1200°F using standard forging techniques. The metal must be protected from the atmosphere during heating but is forged bare. Heating methods described for rolling can be used.

PRESSING

Uranium can be formed by pressing in the gamma range (1470° to 1830°F). The metal is very soft and plastic and deforms under comparatively light loads. The major problem in high-temperature pressing is in finding die materials to withstand the temperature.

It is possible to deep draw uranium to form cups and cylinders. The sheet should be hot rolled at 1110°F, cold rolled to size at 525°F, and then annealed at 1065°F. Dies are designed using the same criteria as those applicable to the drawing of copper. Dies and blanks should be heated to about 345°F. A good lubricant is "liqui-moly" or Acheson "Dag" dispersion #41.

SWAGING

Uranium can be swaged either cold or at temperatures around 930° to 1110°F, and reductions of 10 to 15 percent per pass can be taken. In cold swaging, it may be necessary to anneal after three of four passes.

STRAIGHTENING

Uranium can be straightened by any of several methods including (1) hand hammering, (2) Medart Rotary, (3) Torrington-12 roll straightener, or (4) stretching.

JOINING

While the joining of uranium has received some attention at various times, there is little information on completely satisfactory techniques. Use of any of the conventional techniques is complicated by the reaction of uranium with the atmosphere.

Uranium has been welded using the Heliarc process and the shielded arc-consumable electrode process. The electrode in the latter case was uranium wire. A copper or graphite back-up bar and an argon atmosphere are used.

Joining uranium to uranium by brazing or soldering is handicapped by the formation of brittle compounds between uranium and the joining metals. Some joints have been made by first plating the uranium with silver or nickel and then joining the silver or nickel surfaces together by conventional methods.

MACHINING

Uranium can be machined by most of the conventional methods providing some special precautions are taken. It is advisable to use heavy cuts and relatively high speeds. A lubricant is essential to prevent serious burning of the chips and possibly the finished piece.

SAWING

Uranium can be sawed readily on heavy, power hack saws. A coarse blade (four to six teeth per inch), high pressure, and high speeds are essential. It is necessary to use a heavy flow of lubricant. Lard or mineral-oil type cutting fluids are better than aqueous ones. Under these conditions, a 5-in.-diameter casting can be cut through in 4 min.

TURNING

It is possible to turn uranium either in conventional lathes or with automatic screw machines. Bronze collets are used to hold the material. Only carbide-tipped tools have proven successful, and cutting tools should be shaped to minimize friction and abrasion. Feed and speed rates are determined by the depth of cuts. It is characteristic of uranium that a cutting tool will have a longer life under a heavy cut and a fast feed than under a light cut and a slow feed. Use of an oil coolant rather than a water-soluble oil prolongs tool life and gives a smoother cut.

GRINDING

Grinding can be accomplished using a relatively soft wheel which sheds its grit and continually presents a clean, sharp cutting surface. The surface speed of the wheel should be 5000–6000 ft/min, and the speed of the work should vary from 0.5 to 3.3 ft/min depending on the depth of grind. For this operation, oil is not a suitable lubricant, but water-soluble oil is quite successful. The use of the aqueous lubricant increases the fire hazard of the uranium grindings, and the machine should be cleaned frequently and the uranium dust stored under safe conditions.

MILLING

Uranium can be milled using a high-speed steel cutter. It is advantageous to treat the cutters by deep freezing at -120°F for 2 hr prior to use. A spindle speed of 137 rev/min using a 3-in. slitting saw with a feed of 0.5 ft/min is a recommended procedure. Again an oil coolant is advisable. For milling operations where wide cutters are to be used, it may be desirable to employ Carboly tools.

CORROSION BEHAVIOR

Uranium has very poor corrosion resistance and is generally protected by a coating when used as massive metal in a reactor. Uranium corrodes readily in both air and steam, and

penetration increases rapidly with increasing temperature. Corrosion rates in steam and air are shown in Figs. 1.22.10, 1.22.11, and 1.22.12.

The corrosion rate of uranium in hydrogen-saturated water appears to be constant with respect to time after a brief induction period. Only one over-all type of reaction is involved, and pitting effects are slight. In boiling distilled water, the corrosion rate of uranium is between 0.7 and 3.0 mg/cm²/hr, depending on the purity and heat treatment of the uranium. In aerated distilled water, the initial corrosion rate is somewhat lower than in hydrogen-saturated water, but after long periods of time the corrosion rates approach the panel value. Corrosion rates of uranium in water are shown in Figs. 1.22.13 and 1.22.14.

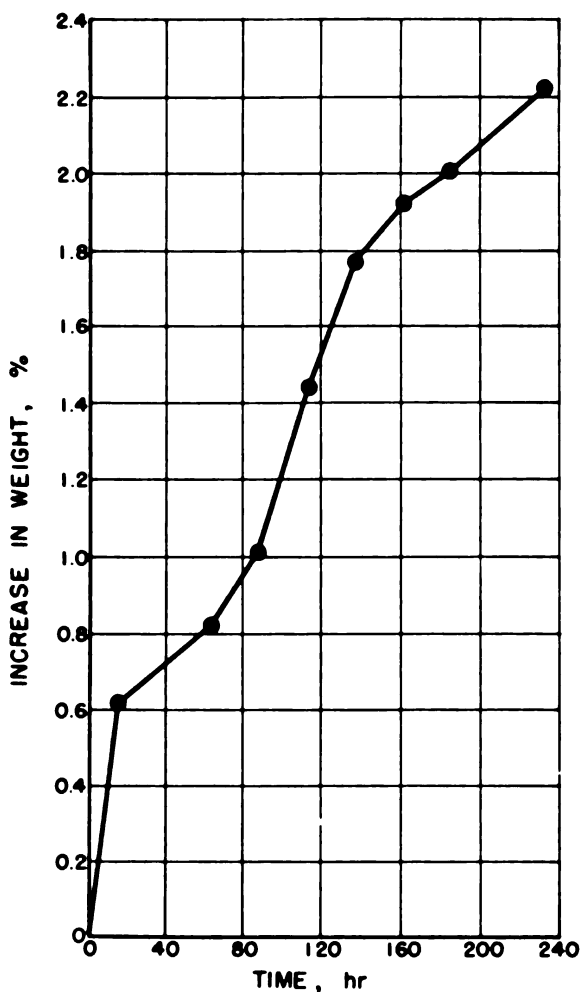


Fig. 1.22.10 — The Percentage Increase in Weight With Time for Uranium in air at 390°F. Reprinted from T. Wathen, Corrosion of Uranium Metal in Air and Steam at Various Temperatures, BR-223-A, May 13, 1943.

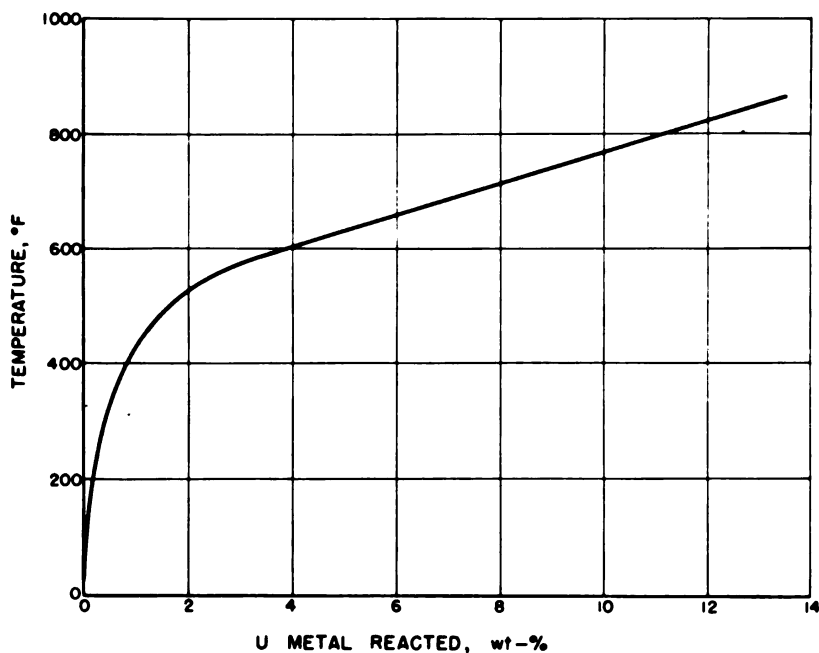


Fig. 1.22.11 — The Oxidation of Uranium in Air for 4-hr Periods from 68° to 930°F. Reprinted from T. Wathen, Corrosion of Uranium Metal in Air and Steam at Various Temperatures, BR-223-A, May 13, 1943.

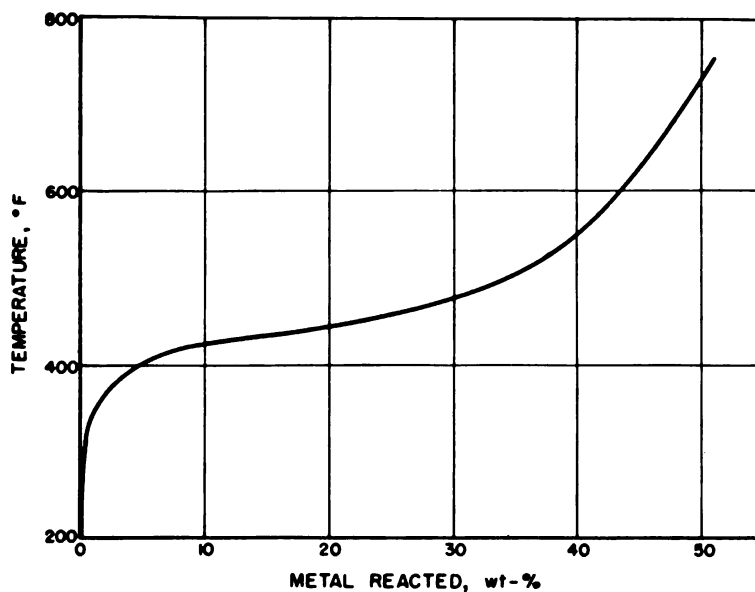


Fig. 1.22.12 — The Action of Steam on Uranium at Various Temperatures. Reprinted from T. Wathen, Corrosion of Uranium Metal in Air and Steam at Various Temperatures, BR-223-A, May 13, 1943.

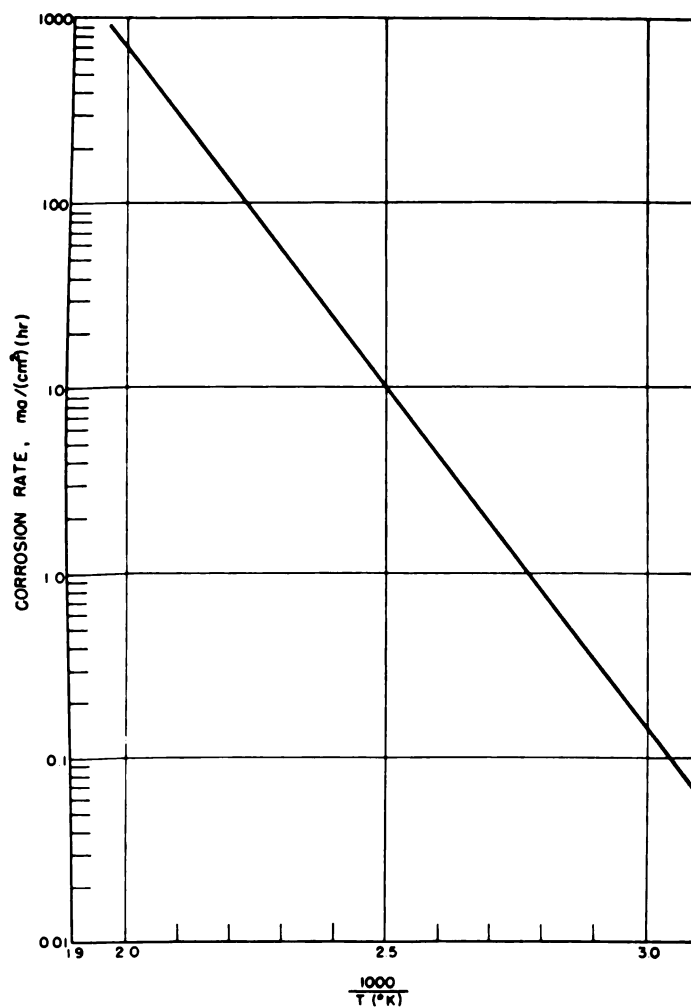


Fig. 1.22.13 — The Corrosion Rate of Uranium in Hydrogen-saturated Water Versus $1/T$. Reprinted from W. A. Mollison, et al., Corrosion of Tuballoy in Distilled Water, University of Chicago, CT-3055, June 23, 1945.

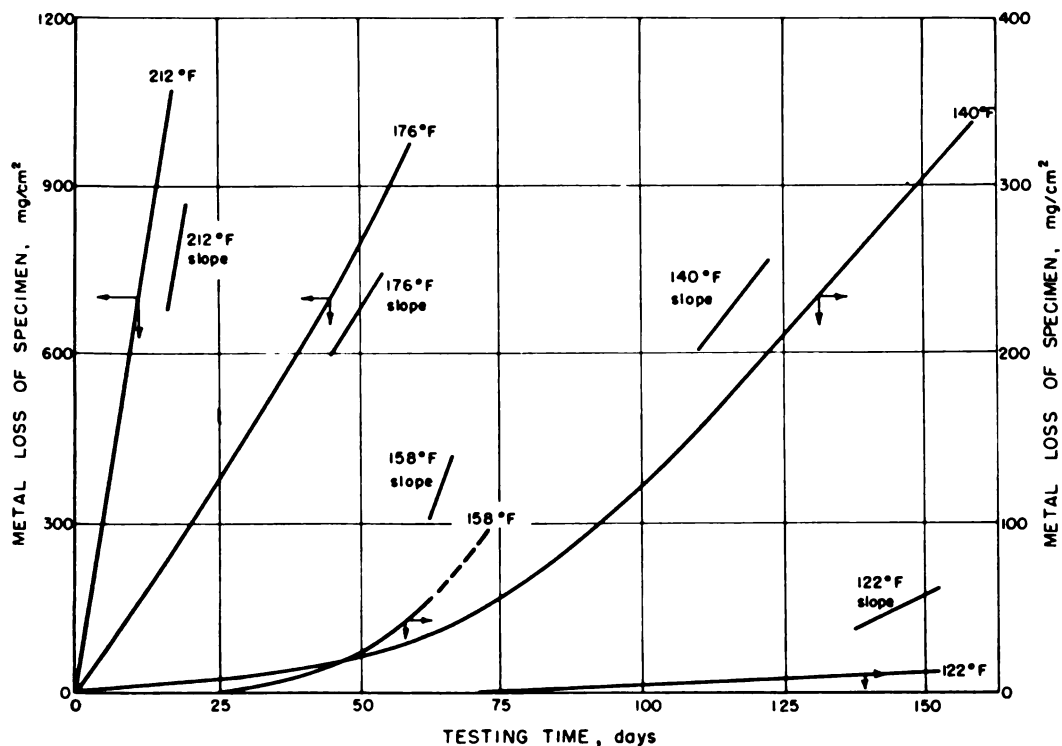


Fig. 1.22.14—Corrosion of Uranium in Aerated-distilled Water. Reprinted from W. A. Mollison, et al., Corrosion of Tuballoy in Distilled Water, University of Chicago, CT-3055, June 23, 1945.

PROTECTIVE TECHNIQUES

The poor corrosion resistance of uranium in reactor coolants has made the development of protective coatings most important. Considerable effort has been expended on all the conventional coating methods with varying success.

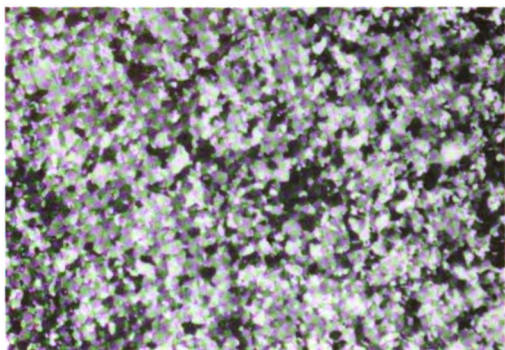
Uranium can be electroplated with a number of metals by using conventional plating baths, but cleaning the surface prior to plating has offered some difficulty. Roll cladding of uranium with a number of metals has been perfected, and, for some applications, uranium is protected simply by jacketing in aluminum cans.

METALLOGRAPHY

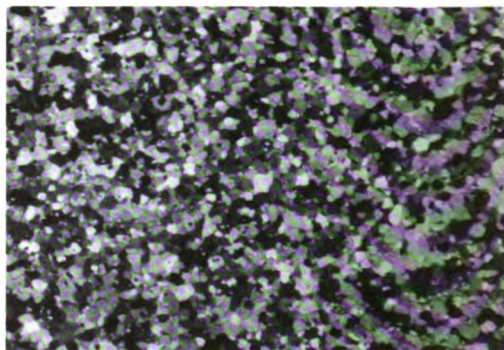
Typical structures obtained by several laboratories on a selected series of specimens are shown in Fig. 1.22.15. Figure 1.22.16 shows a standard grain-size chart for uranium.

The relatively soft, smeary quality of uranium metal makes metallographic polishing by conventional mechanical techniques very difficult. Adequate electropolishing methods have been developed, however.

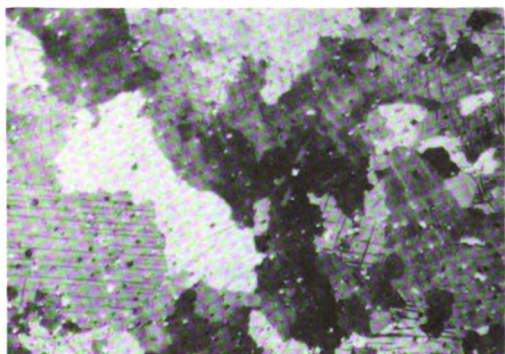
Uranium-metallographic specimens can be rough cut by any of the usual methods, including sawing, abrasive cutting, and machining. Preliminary and final grinding are done on abrasive-grit papers. Grinding should be done wet with water or kerosene and paraffin



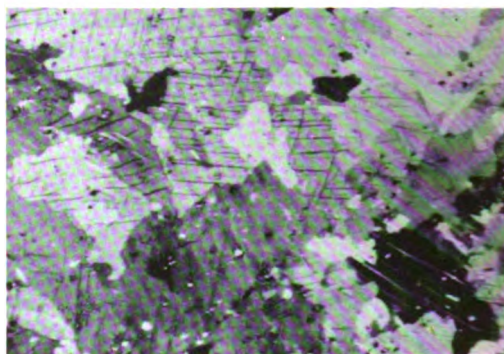
Rolled at 750°F



1 hr anneal at 1250°F, furnace cool

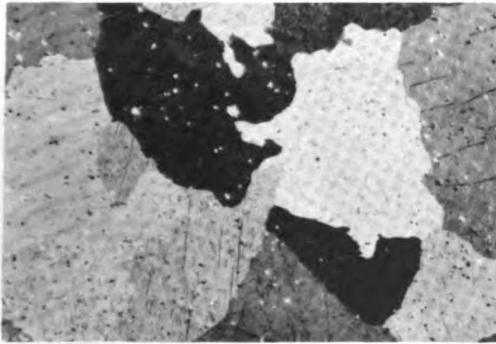


1 min at 1290°F, water quench

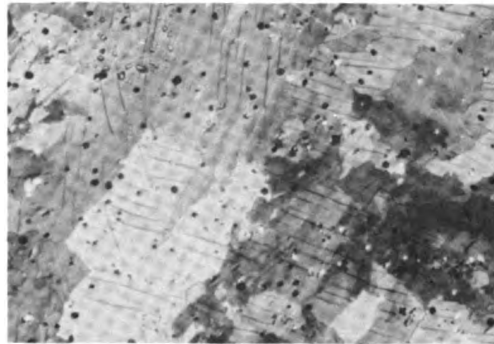


1 hr at 1290°F, water quench

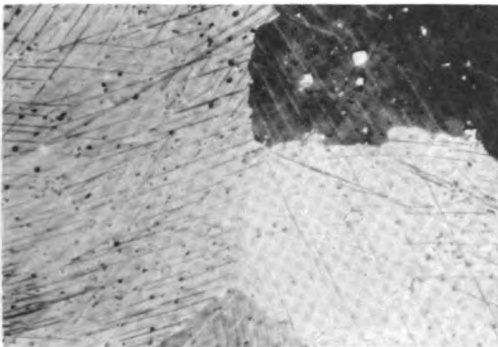
Fig. 1.22.15 — See facing page for legend.



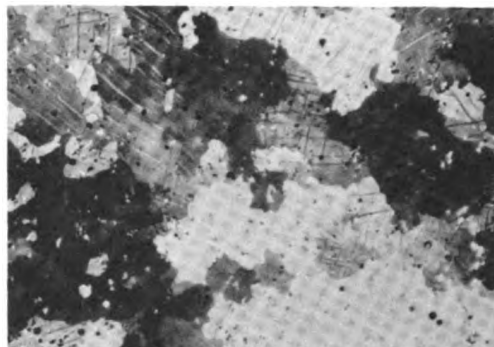
1 hr at 1290°F, furnace cool



1 hr at 1470°F, water quench



1 hr at 1470°F, furnace cool



1 hr at 1290°F, water quench
4 hr at 1250°F, furnace cool

Fig. 1.22.15— Typical Microstructures of Uranium After Indicated Heat Treatments. Submitted by Battelle Memorial Institute, July 1, 1952. All photomicrographs at 100X using polarized light.

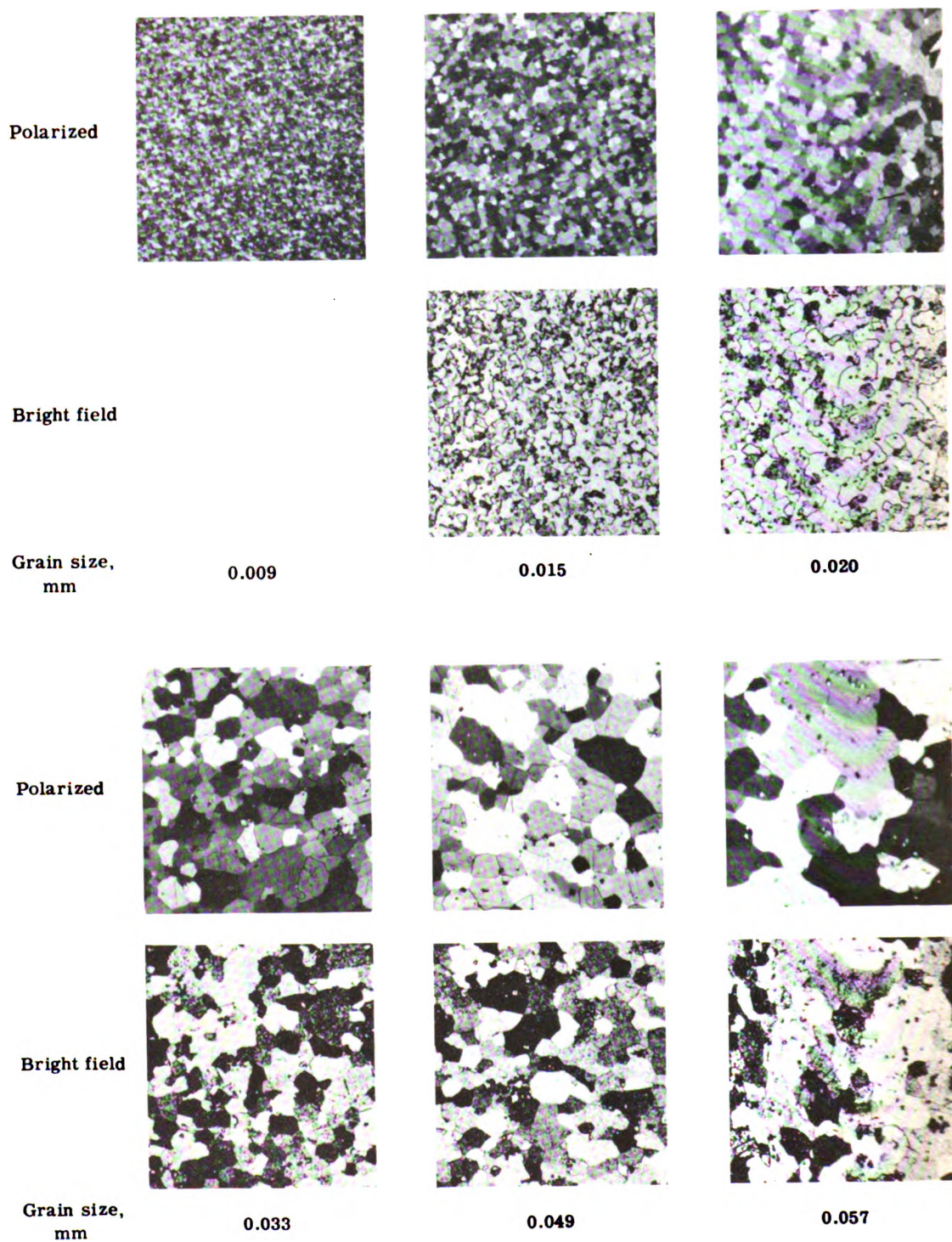


Fig. 1.22.16—See facing page for legend.

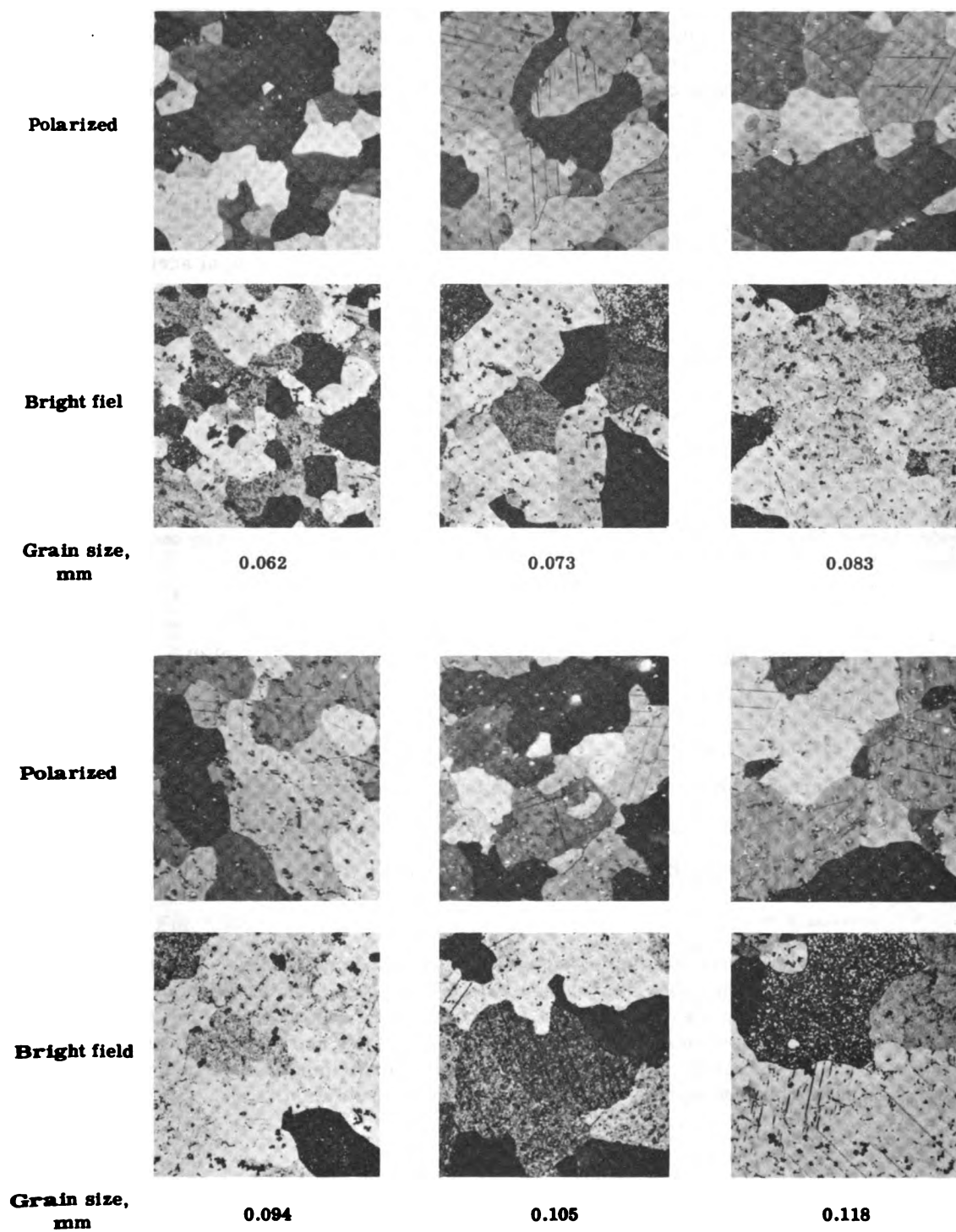


Fig. 1.22.16 — A Standard Grain-size Chart for Uranium. Submitted by Battelle Memorial Institute, July 1, 1952.

as lubricants. Hand grinding is recommended on the papers. Some metallographers prefer to use one wet, final-polishing wheel prior to the electropolish. Such a wheel might use an abrasive of "Linde B" on Buehler Selvyt cloth.

Two types of electrolytic-polishing baths are used generally for uranium as follows:

Bath	1	2
Composition	5 parts phosphoric acid 5 parts ethylene glycol 8 parts alcohol	50 gm CrO_3 solid 60 cm^3 water 180 cm^3 glacial acetic acid
Bath temperature	70°F	45°F
Current density	30-50 ma/sq in.	4-8 amp/sq in.
Cathode material	Stainless steel	Stainless steel
Time for polishing	5-15 min	5-30 sec

The anisotropic qualities of uranium make it possible to observe the alpha grain boundaries on unetched metal by the use of polarized light. However, to examine the specimen under bright-field illumination, it is advantageous to delineate the grains by means of an etch.

Bath	1	2
Composition	2% citric acid 0.5% nitric acid 92.5% water	25 gm CrO_3 (solid) 30 cm^3 water 300 cm^3 glacial acetic acid
Bath temperature	75°F	120°F
Current density	75 ma/sq in.	4-6 amp/sq in.
Cathode material	Stainless steel	Stainless steel
Time for etching	10 min	1-3 min

Polishing of semiporous uranium compacts produced at some stages in the powder-metallurgy process requires a special mechanical technique. The sample is dry polished through 3/0 paper. It is then polished for a short time on a silk wheel and for 2 to 3 min on a velvet-covered disc using Linde-A powder sprinkled dry and lubricated with a solution of 60 cm^3 HF, 30 cm^3 HNO_3 , and 60 cm^3 H_2O . After final polishing, the surface of the specimen is cleaned by swabbing with a nitric- and acetic-acid solution.

URANIUM ALLOYS

Since uranium is relatively weak and has poor corrosion resistance, there has been considerable interest in alloying to overcome these shortcomings. Alloying of uranium is also desirable for nuclear reasons.

Constitutional diagrams for uranium with a number of elements have been developed. They are shown in alphabetical order of the added element in Figs. 1.22.17 through 1.22.40.

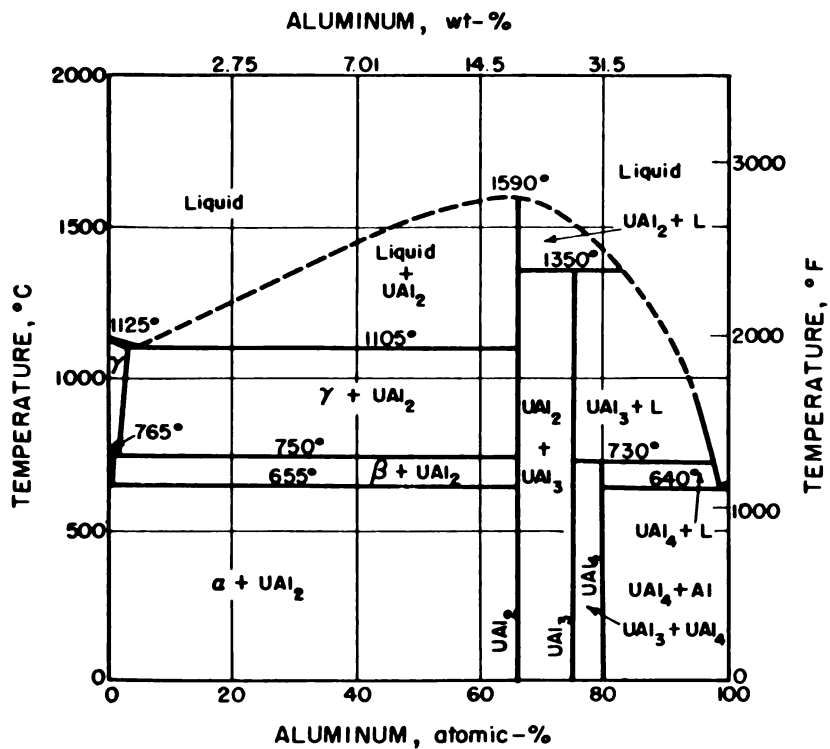


Fig. 1.22.17 — The Constitutional Diagram of the System Uranium-Aluminum. Reprinted from R. W. Buzzard and H. E. Cleaves, The Binary Alloys of Uranium, J. Met. and Cer., TID-65, July 1948.

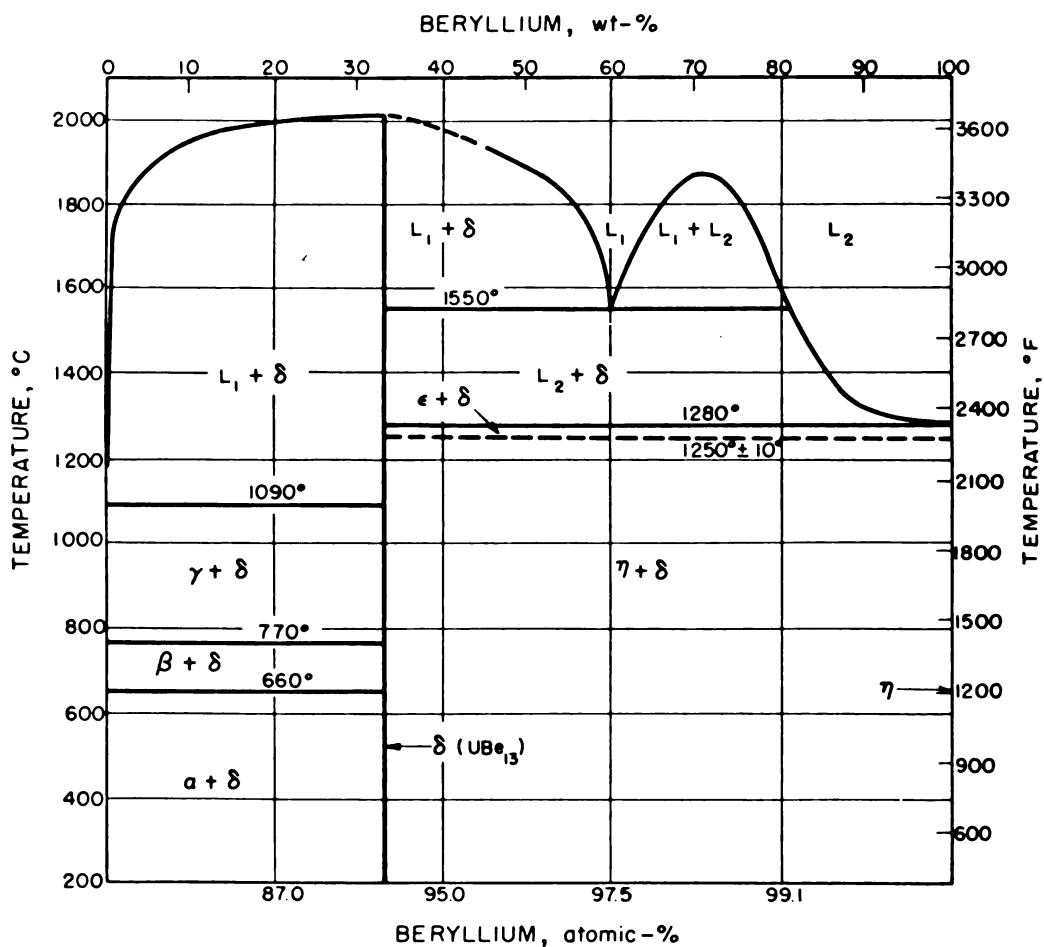


Fig. 1.22.18 — The Constitutional Diagram of the System Uranium-Beryllium.
Submitted by Battelle Memorial Institute, July 1, 1952.

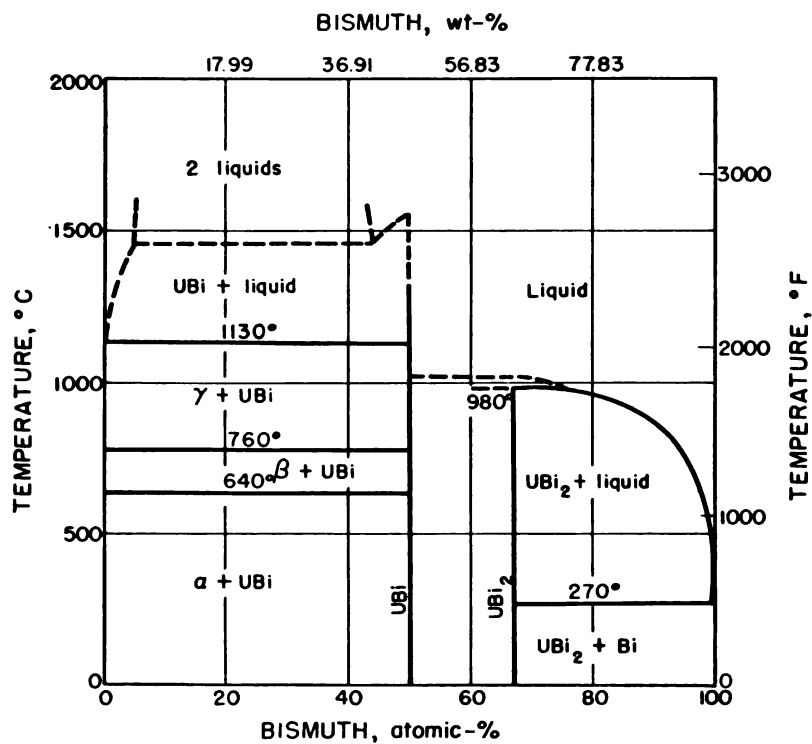


Fig. 1:22.19—The Constitutional Diagram of the System Uranium-Bismuth. Reprinted from R. W. Buzzard and H. E. Cleaves, The Binary Alloys of Uranium, J. Met. and Cer., TID-65, July 1948.

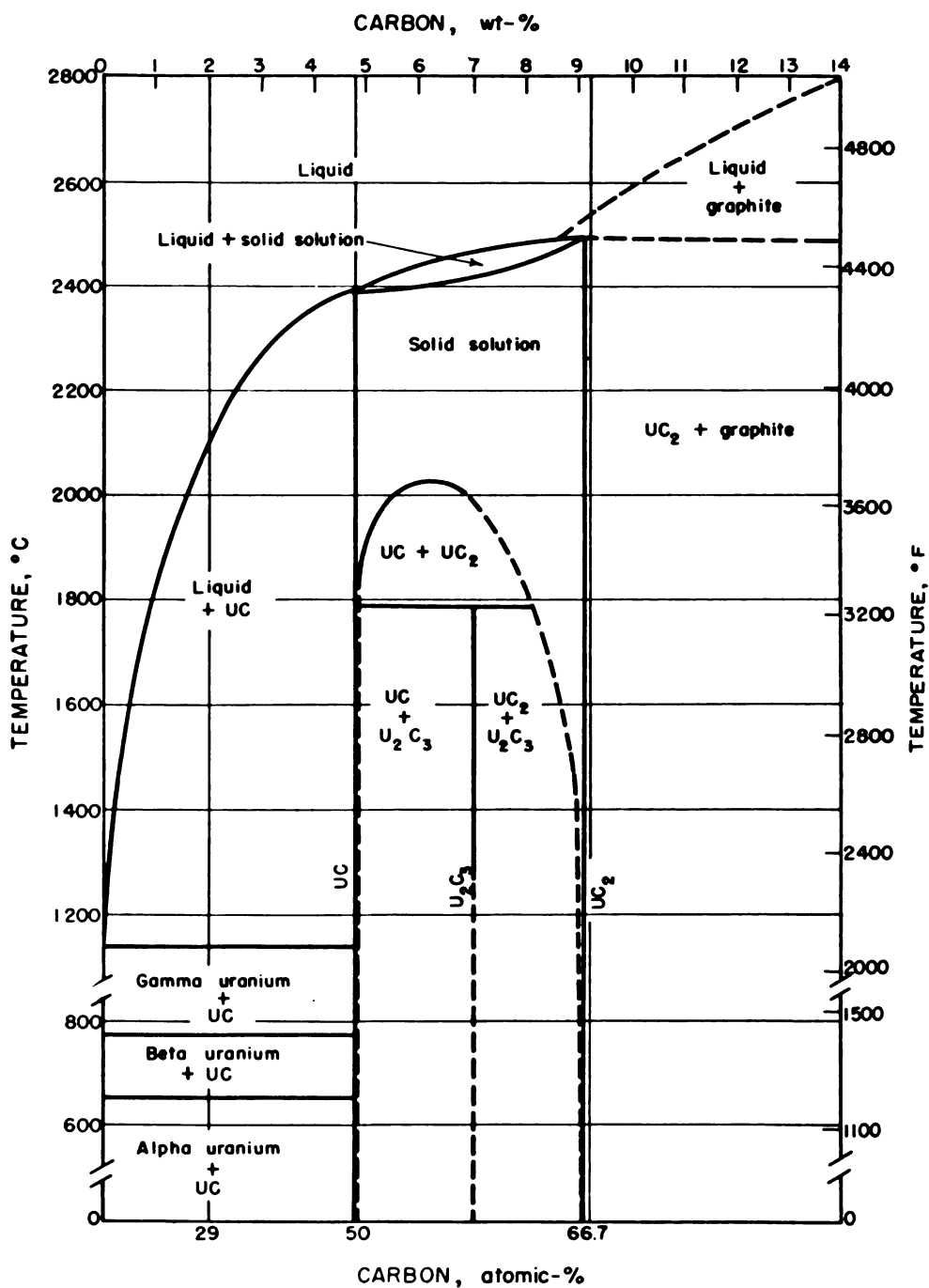


Fig. 1.22.20 — The Constitutional Diagram of the System Uranium-Carbon. Reprinted from M. W. Mallett, et al., *The Uranium-Carbon System*, BMI-63, Apr. 1, 1951.

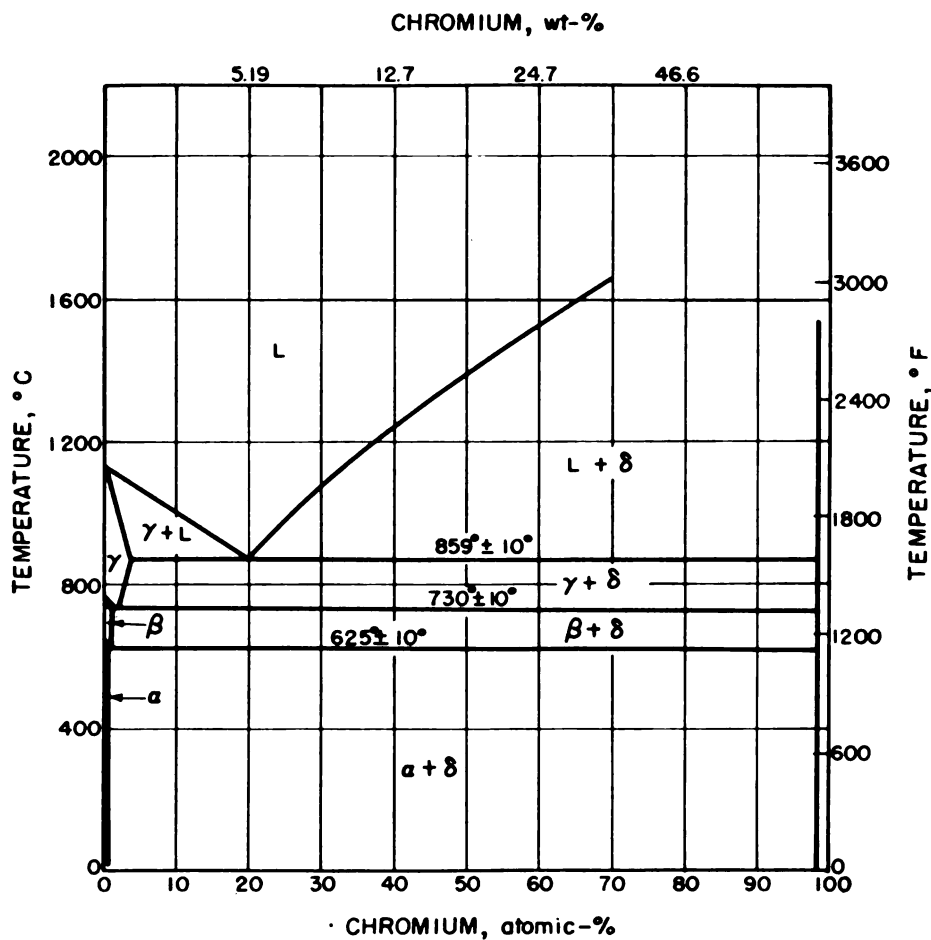


Fig. 1.22.21—The Constitutional Diagram of the System Uranium-Chromium.
Submitted by Battelle Memorial Institute, July 1, 1952.

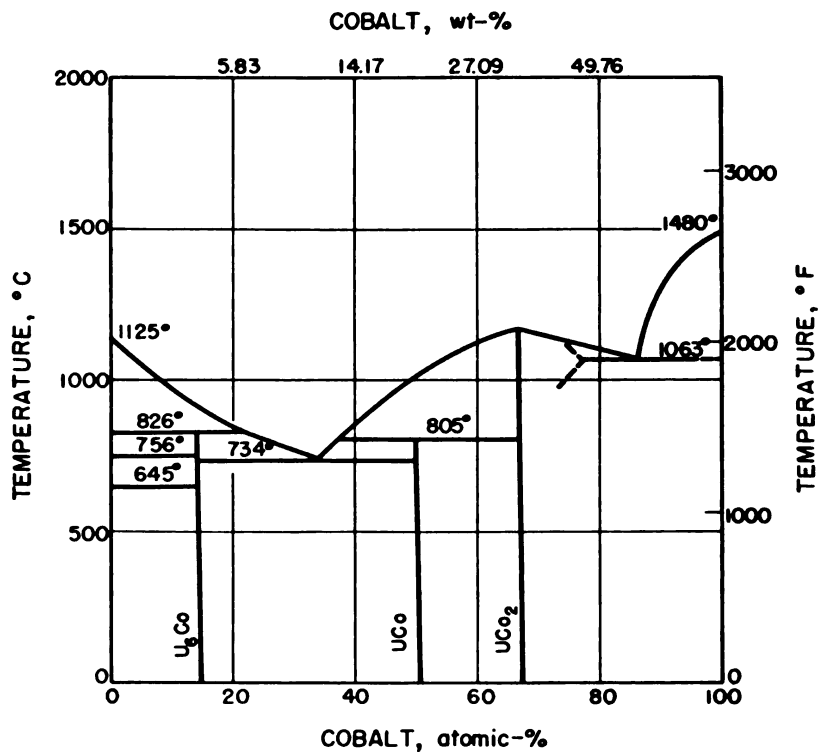


Fig. 1.22.22 — The Constitutional Diagram of the System Uranium-Cobalt. Reprinted from R. W. Buzzard and H. E. Cleaves, The Binary Alloys of Uranium, J. Met. and Cer., TID-65, July 1948.

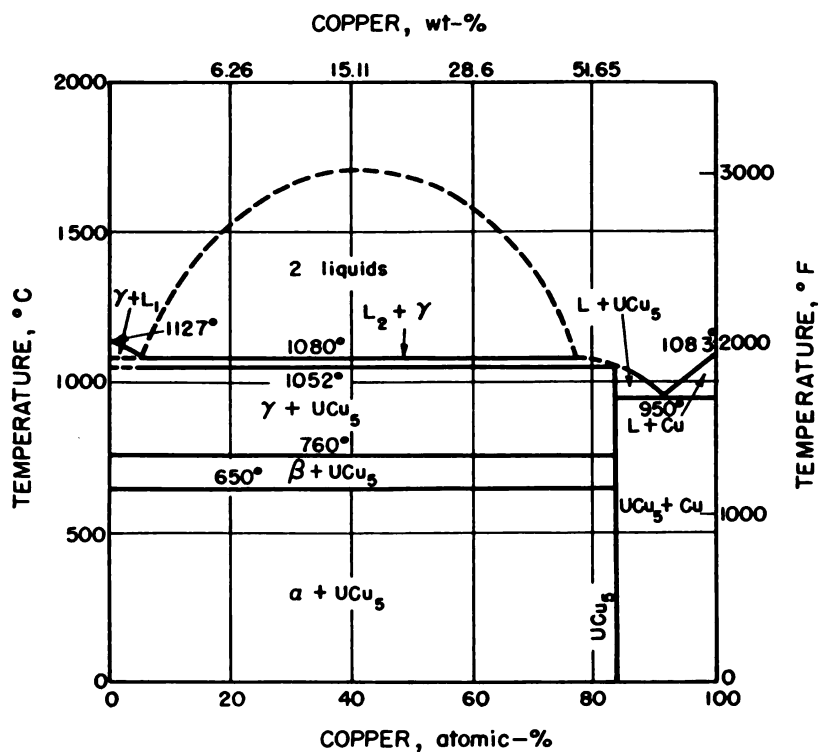


Fig. 1.22.23 — The Constitutional Diagram of the System Uranium-Copper. Reprinted from R. W. Buzzard and H. E. Cleaves, *The Binary Alloys of Uranium*, J. Met. and Cer., TID-65, July 1948.

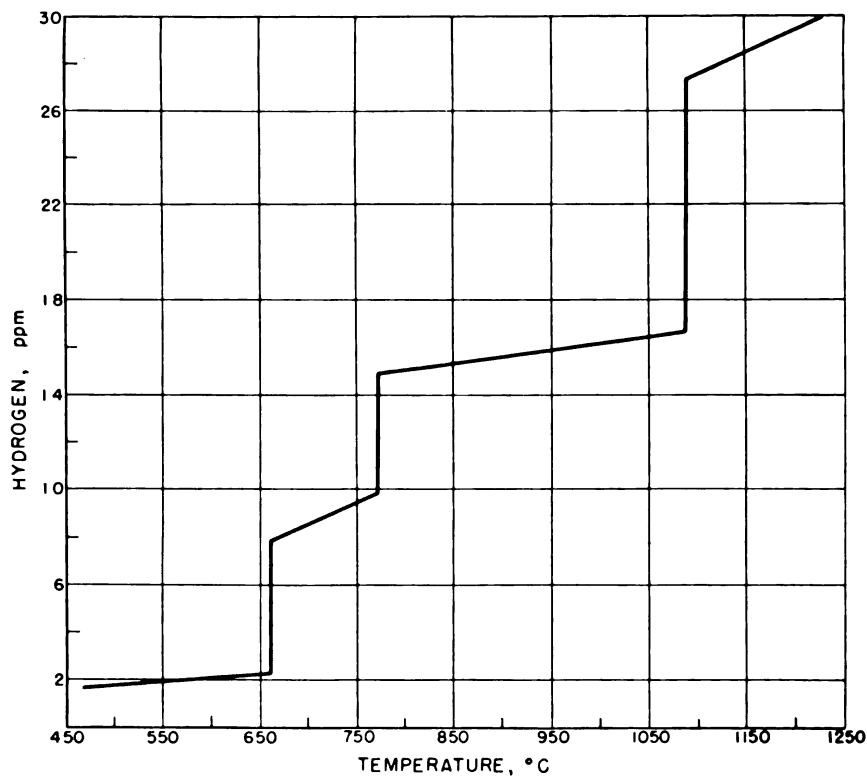


Fig. 1.22.24 — The Solubility of Hydrogen in Uranium in Equilibrium With Hydrogen at Atmospheric Pressure. Reprinted from Progress Report on Metallurgy of Tuballoy, BMI-HWR-14, CT-1388, Feb. 10, 1944.

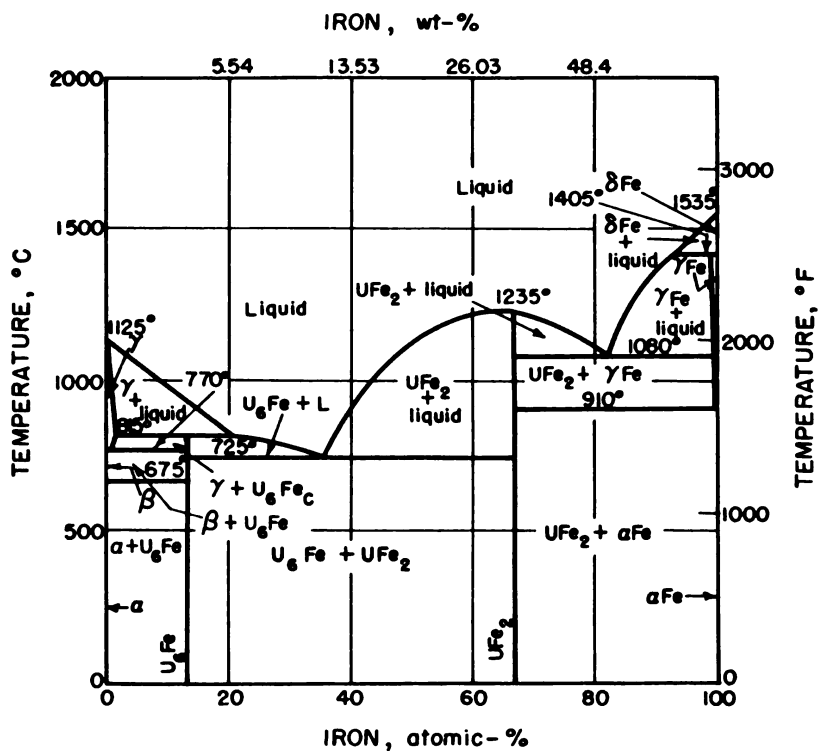


Fig. 1.22.25—The Constitutional Diagram of the System Uranium-Iron. Reprinted from R. W. Buzzard and H. E. Cleaves, *The Binary Alloys of Uranium*, J. Met. and Cer., TID-65, July 1948.

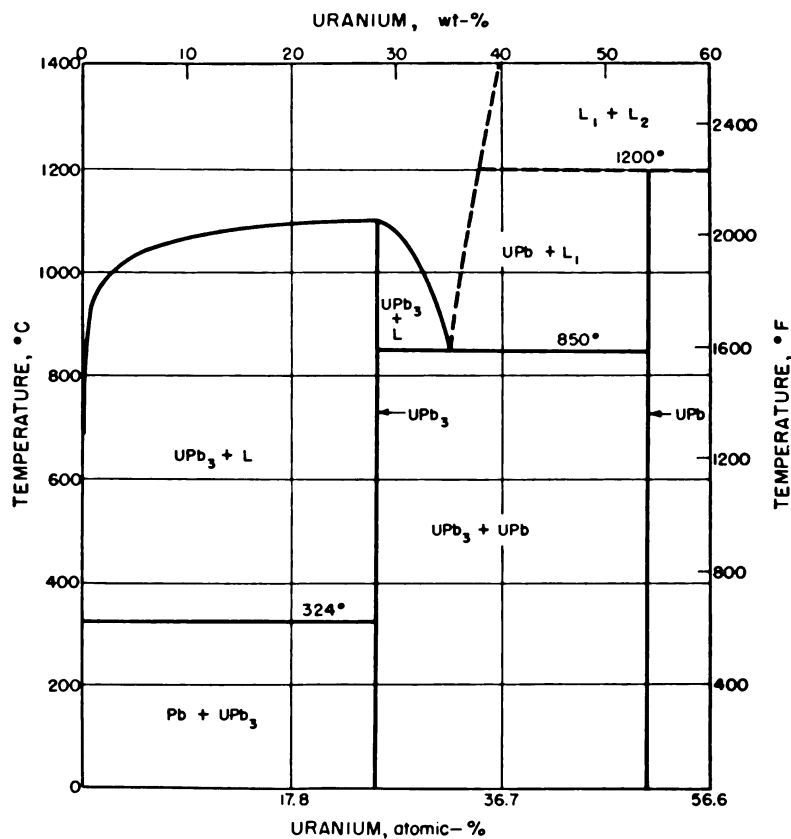


Fig. 1.22.26 —The Constitutional Diagram of the System Lead-Uranium. Reprinted from Classified Progress Report of the Reactor Science and Engineering Dept., Jan. 1 - Mar. 31, 1950, BNL-52, June 1950.

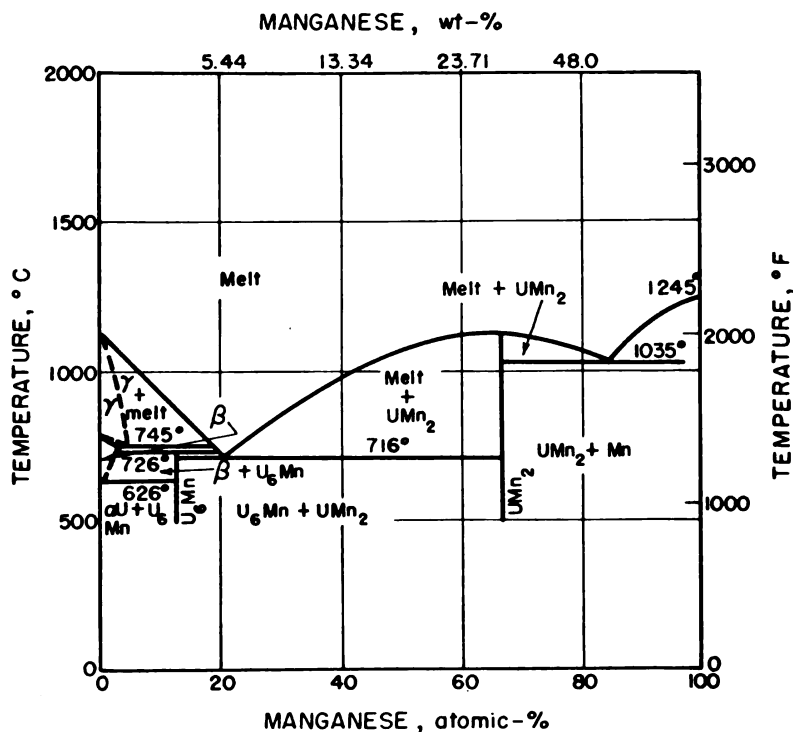


Fig. 1.22.27— The Constitutional Diagram of the System Uranium-Manganese. Reprinted from R. W. Buzzard and H. E. Cleaves, The Binary Alloys of Uranium, J. Met. and Cer., TID-65, July 1948.

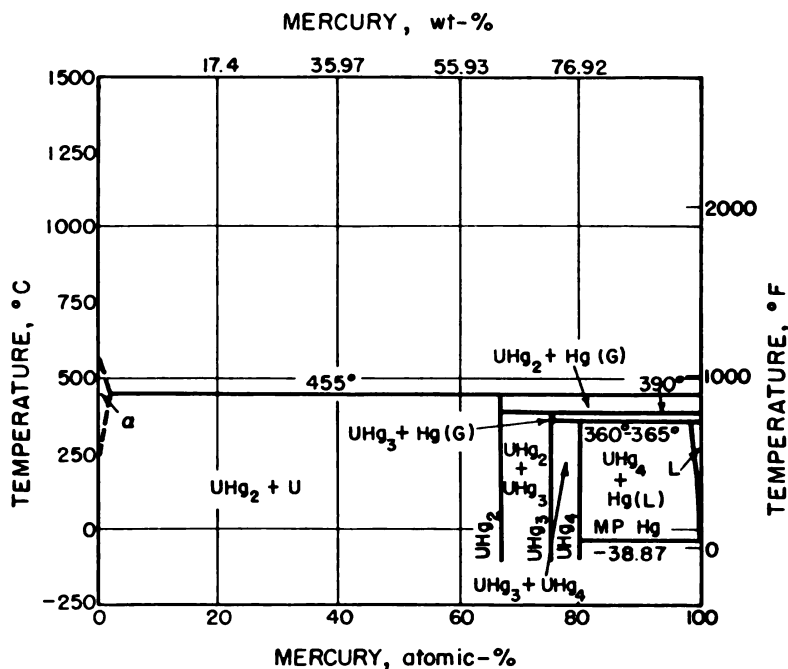


Fig. 1.22.28— The Constitutional Diagram of the System Uranium-Mercury. Reprinted from R. W. Buzzard and H. E. Cleaves, The Binary Alloys of Uranium, J. Met. and Cer., TID-65, July 1948.

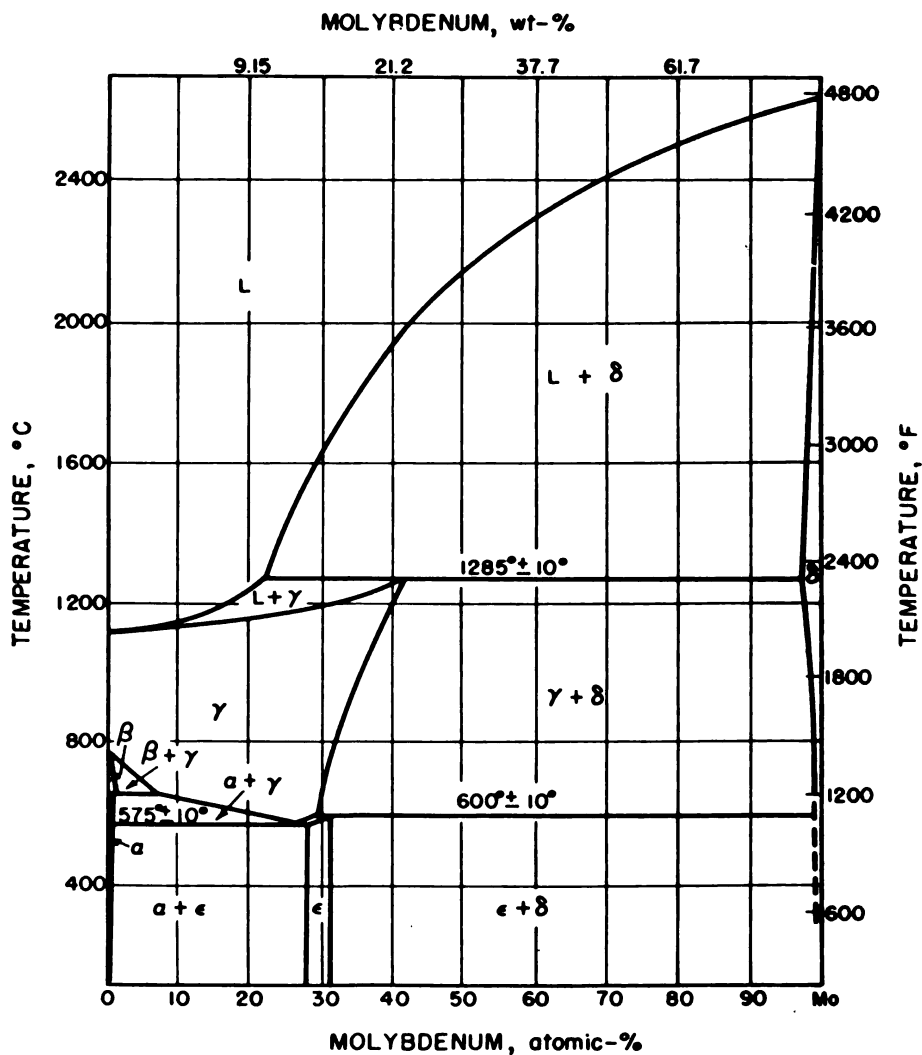


Fig. 1.22.29 — The Constitutional Diagram of the System Uranium-Molybdenum. Submitted by Battelle Memorial Institute, July 1, 1952.

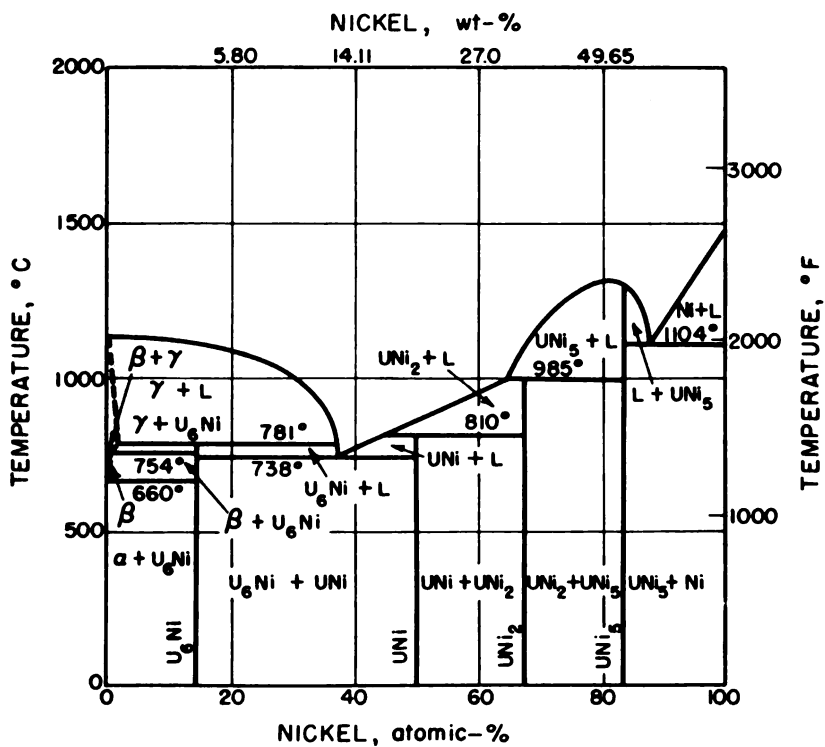


Fig. 1.22.30—The Constitutional Diagram of the System Uranium-Nickel. Reprinted from R. W. Buzzard and H. E. Cleaves, The Binary Alloys of Uranium, J. Met. and Cer., TID-65, July 1948.

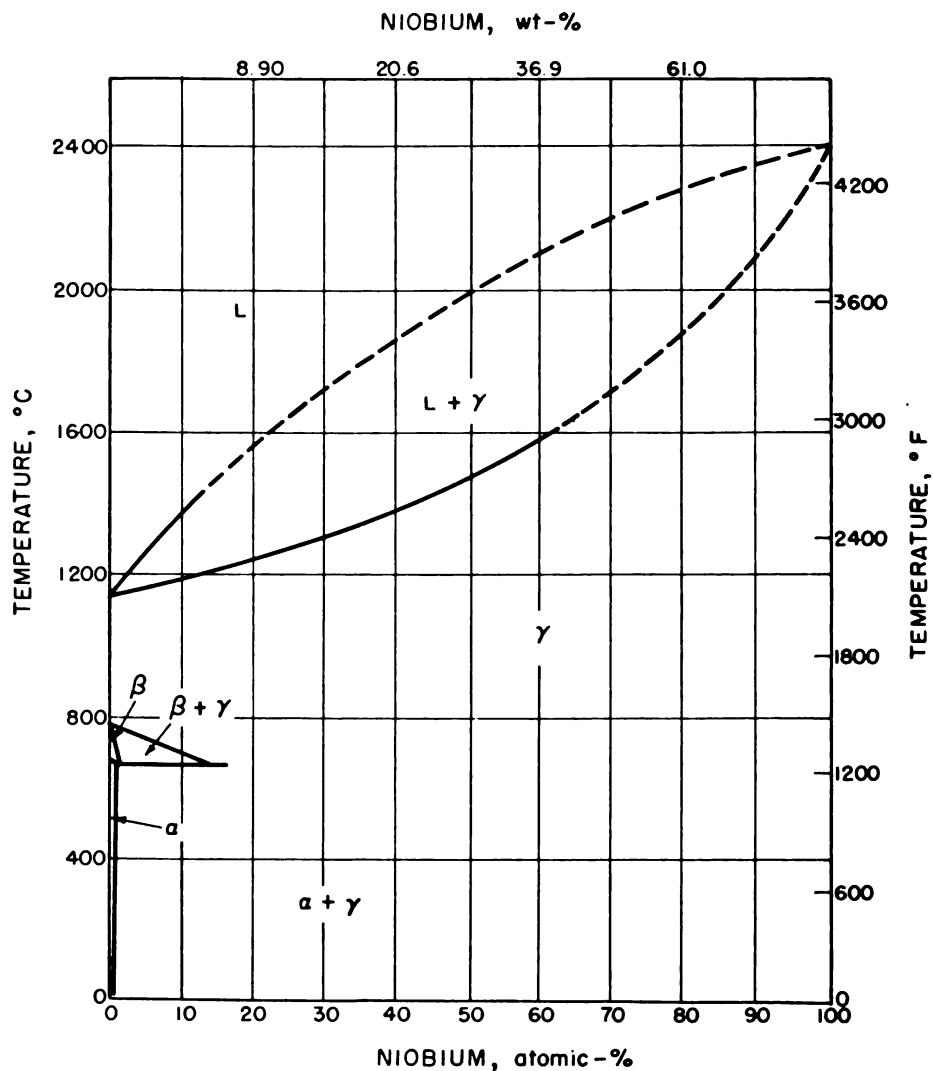


Fig. 1.22.31 — The Constitutional Diagram of the System Uranium-Niobium. Submitted by Battelle Memorial Institute, July 1, 1952.

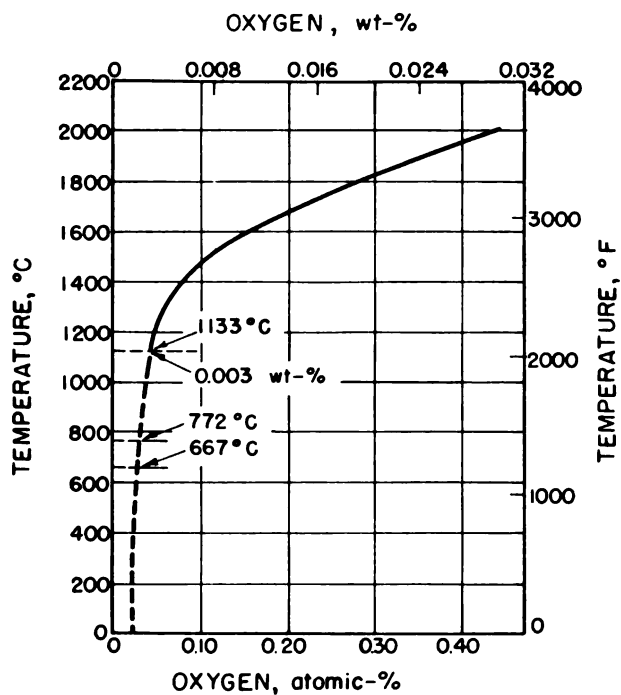


Fig. 1.22.32 — The Solubility of Oxygen in Uranium. Reprinted from J. J. Katz and Eugene Rabinowitch, *The Chemistry of Uranium*, NNEs, Division VIII, Vol 5, Chapter 4, McGraw-Hill, 1951.

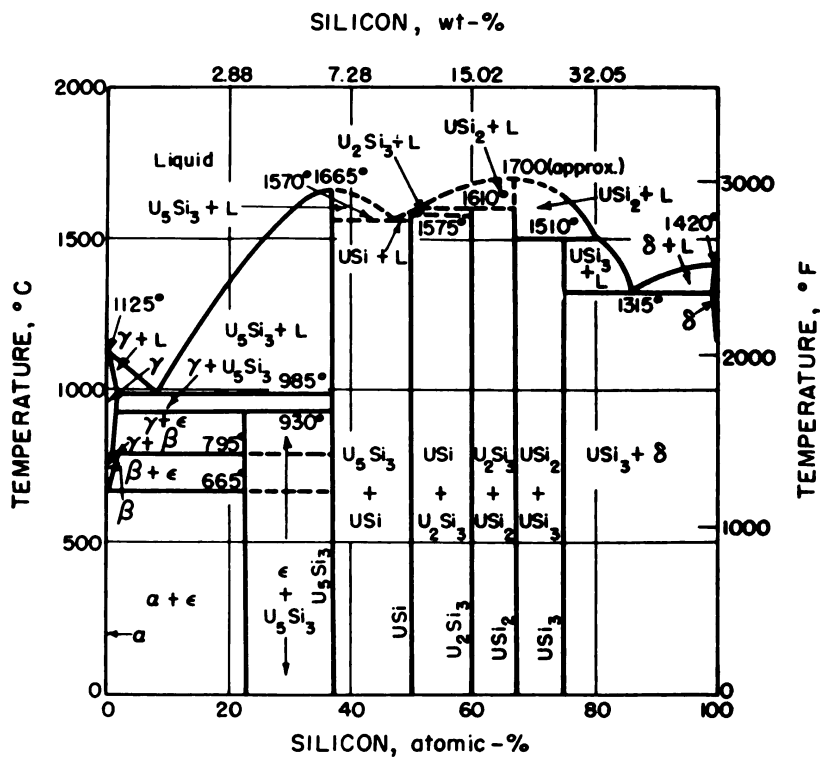


Fig. 1.22.33 — The Constitutional Diagram of the System Uranium-Silicon. Reprinted from R. W. Buzzard and H. E. Cleaves, *The Binary Alloys of Uranium*, J. Met. and Cer., TID-65, July 1948.

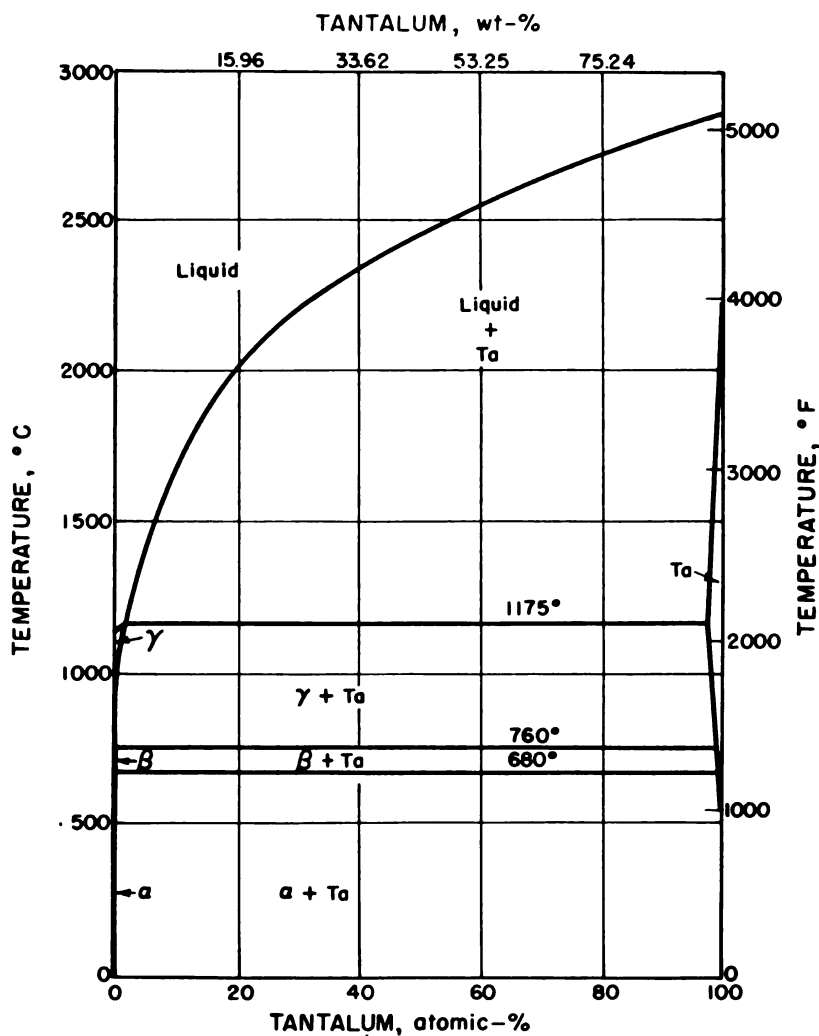


Fig. 1.22.34—The Constitutional Diagram of the System Uranium-Tantalum. Reprinted from R. W. Buzzard and H. E. Cleaves, *The Binary Alloys of Uranium*, J. Met. and Cer., TID-65, July 1948.

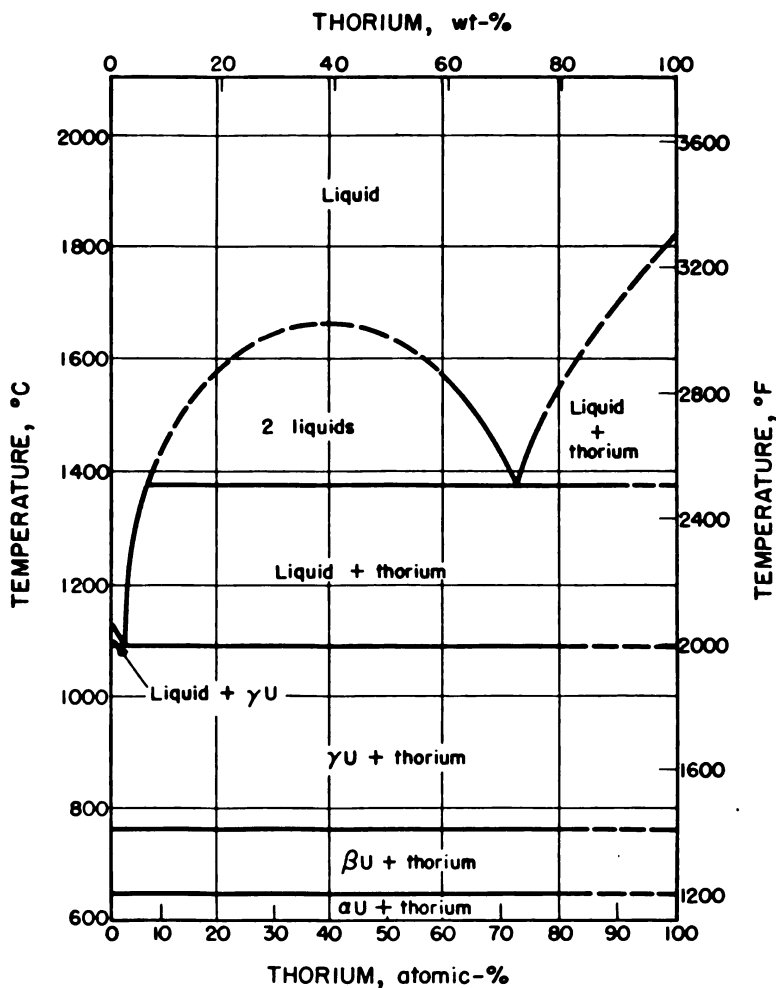


Fig. 1.22.35—The Constitutional Diagram of the System Uranium-Thorium. Submitted by Battelle Memorial Institute, July 1, 1952.

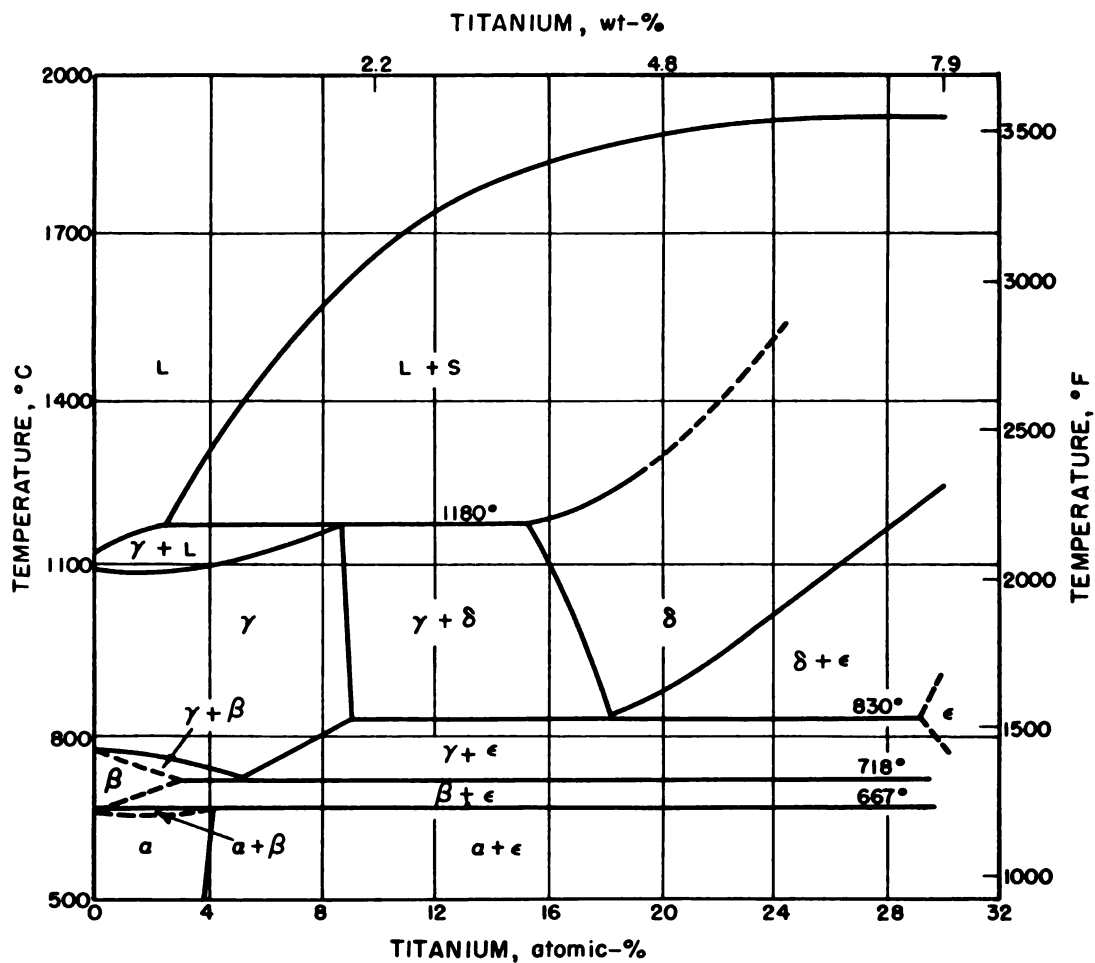


Fig. 1.22.36 — The Constitutional Diagram of the System Titanium-Uranium. Data supplied by National Bureau of Standards.

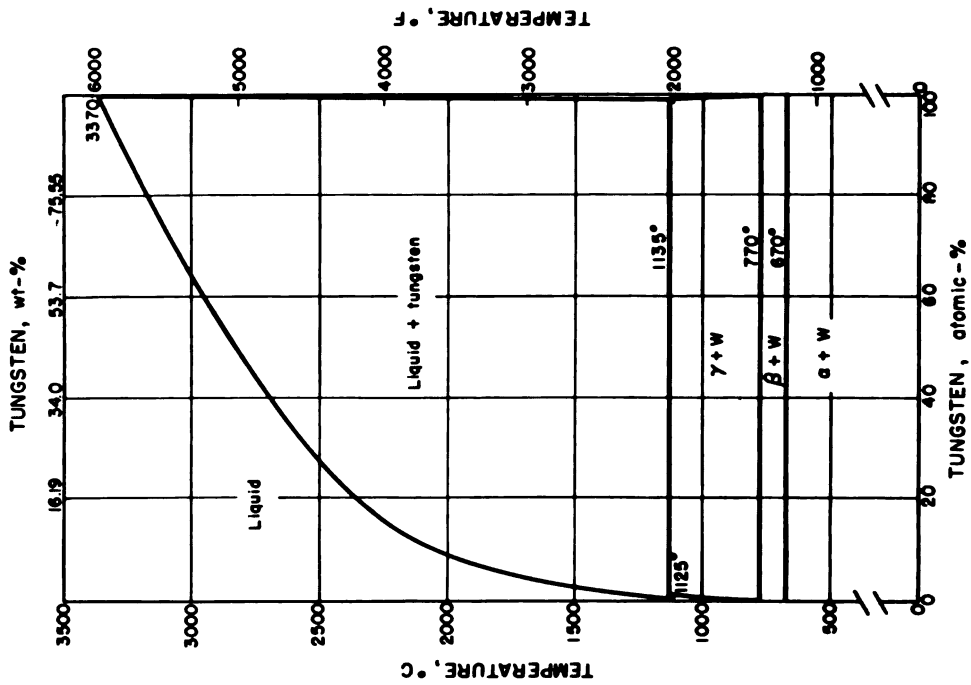


Fig. 1.22.38 — The Constitutional Diagram of the System Uranium-Tungsten. Reprinted from R. W. Buzzard and H. E. Cleaves, *The Binary Alloys of Uranium, J. Met. and Cer.*, TID-65, July 1948.

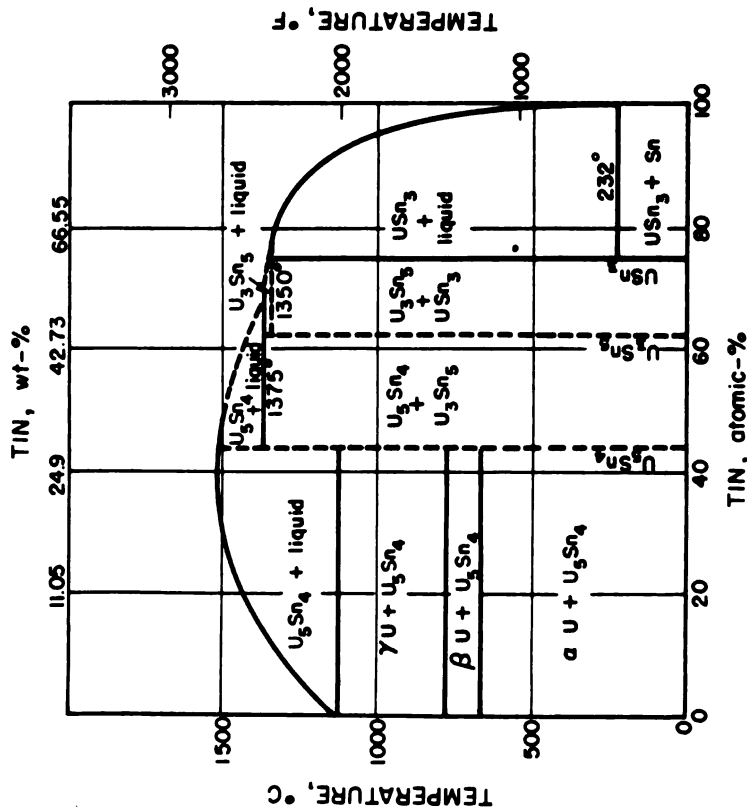


Fig. 1.22.37 — The Constitutional Diagram of the System Uranium-Tin. Reprinted from R. W. Buzzard and H. E. Cleaves, *The Binary Alloys of Uranium, J. Met. and Cer.*, TID-65, July 1948.

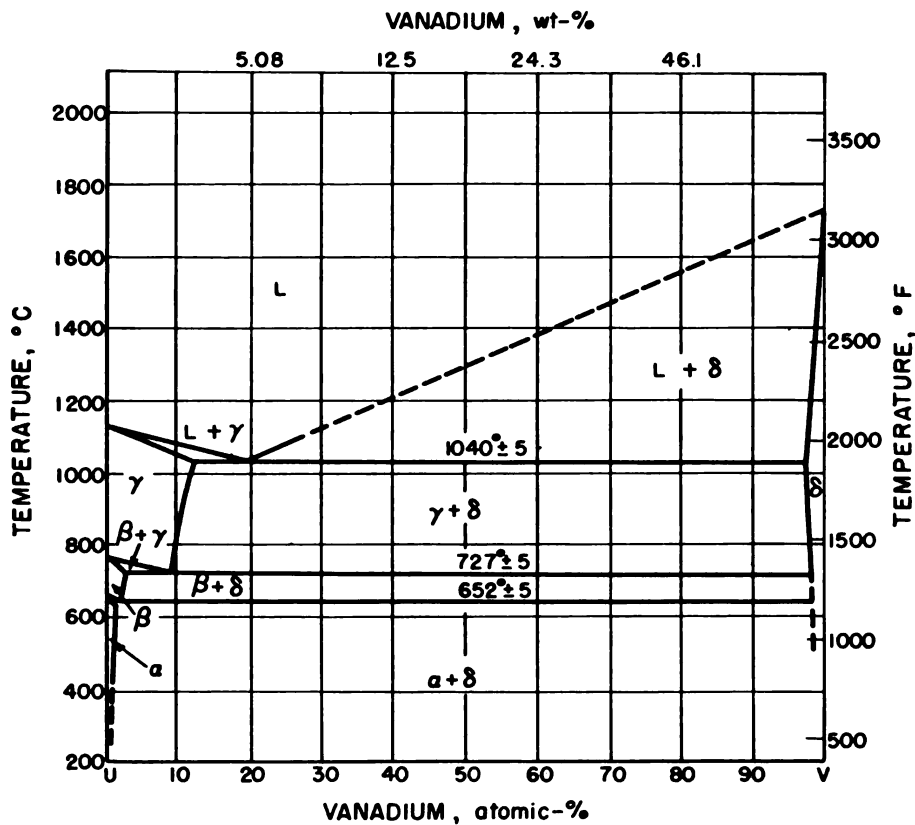


Fig. 1.22.39—The Constitutional Diagram of the System Uranium-Vanadium.
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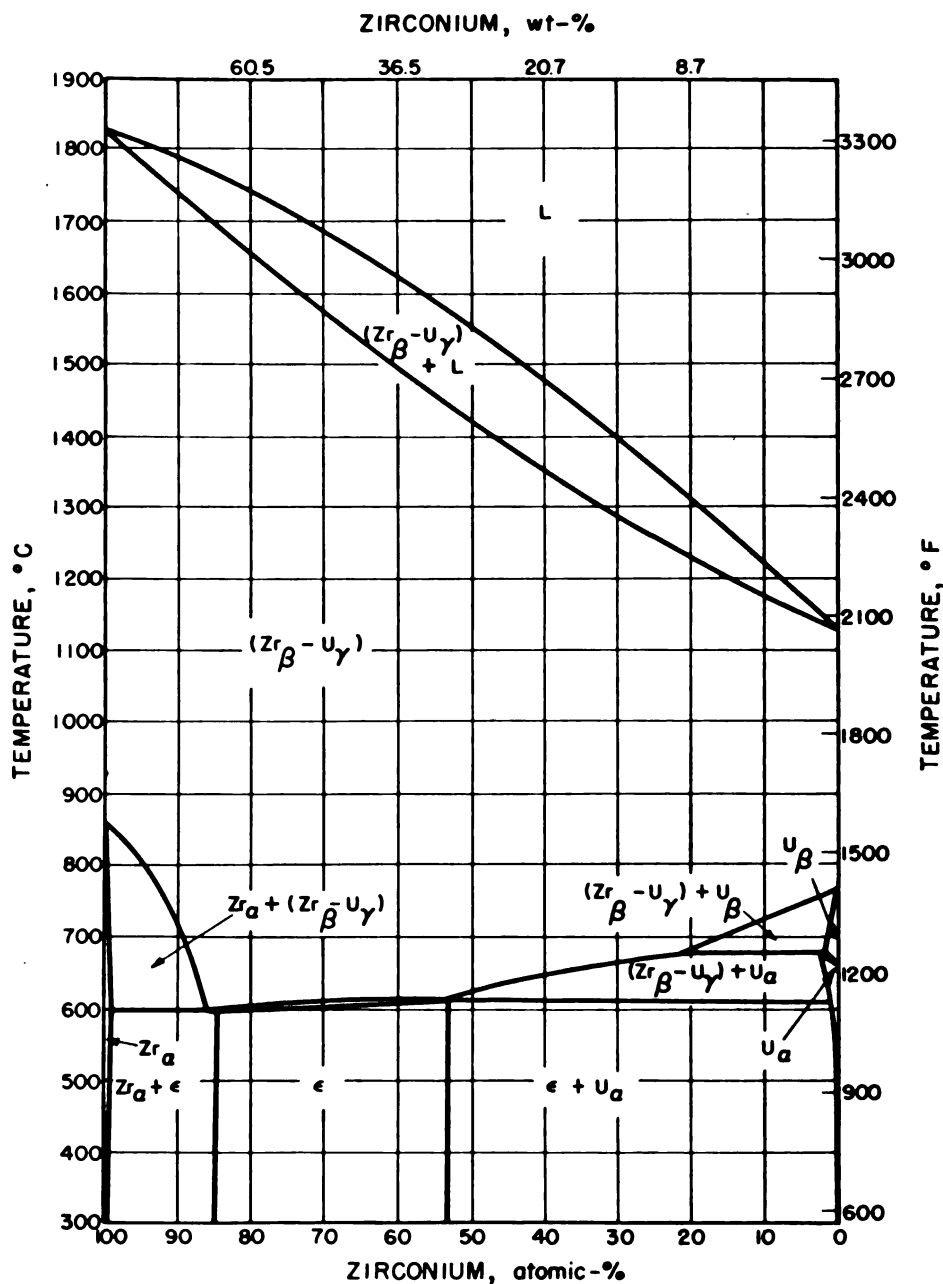


Fig. 1.22.40— The Constitutional Diagram of the System Uranium-Zirconium. Submitted by Battelle Memorial Institute, July 1, 1952.

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CHAPTER 1.23

Vanadium and Its Alloys

J. R. Keeler

Vanadium is the most recent rare metal to become available in fabricated form and in appreciable quantities. Although the element was discovered over 150 years ago, the metal is extremely difficult to prepare with sufficient purity to be ductile, and only small quantities of ductile metal had been made before 1950. The metal is now available in 100 lb/day quantities at a price of approximately \$30/lb.

REACTOR APPLICATION

Vanadium has a low fission-neutron cross section, and its inelastic scattering cross section is also quite small. These favorable nuclear properties coupled with vanadium's high melting point, ductility, and good physical properties make the metal of particular interest as a structural material for fast reactors. Favorable alloying characteristics with uranium also make the metal of interest as a diluent, although the transport cross section is small. The thermal cross section of vanadium is large, however, and its usefulness in thermal reactors is limited.

ABUNDANCE AND AVAILABILITY

Vanadium is the fourteenth most abundant element in the earth's crust and is estimated to occur in amounts equal to the sum of the concentrations of copper, zinc, and lead, or about 160 ppm. The metal is widely distributed; however, only a few massive deposits have been found. The principal deposits in the United States occur in Colorado, Utah, and Arizona. Deposits also occur in Mina Ragra, Peru, in Northern Rhodesia, and in Southwest Africa.

The ores in the United States contain principally carnotite and roscoelite. Carnotite has been the chief source of vanadium, and its ores are now worked for both its uranium and vanadium contents. Carnotite is a uranium-potassium vanadate containing approximately 54 percent UO_2 and 18 percent V_2O_5 .

Small quantities of vanadium have been recovered commercially from phosphate rocks, iron ores, chrome ores, magnetite beach sands, caustic soda solutions used in aluminum refining, soot from smokestacks carrying the fume from certain oils, and ash derived from oil-bearing shales. The principal source of the element, however, has been the western carnotite ores, and production from this source has increased greatly as the result of increased uranium mining. In a typical year, 95 percent of the vanadium

production is consumed by the steel industry. The 1951 production of vanadium concentrates was about twice the normal annual consumption. In addition, vanadium equivalent to one-third the annual consumption was imported. From these figures, it is readily seen that a considerable amount of vanadium is being stockpiled and that the concurrent development of new uses is not only desirable but necessary.

The major use of vanadium is as ferrovanadium for the production of alloy steels. Only about 5 percent of the annual consumption is used for nonmetallurgical purposes, such as catalysts, ceramic glazes, and driers in paint, ink, and pigments. Production of small quantities of pure, ductile metal for experimental purposes was started in 1950 at a cost of approximately \$30/lb. With present facilities, production of 100 lb of massive ductile vanadium per day is reported to be feasible.

EXTRACTION AND PURIFICATION

The production of pure vanadium in quantities greater than a few grams has proven arduous. The metal is highly reactive and has a high melting point. In addition, its properties, particularly its ductility, are extremely sensitive to small quantities of impurities.

Small quantities of high-purity ductile metal have been produced by the thermal decomposition of vanadium iodide and by the reduction of vanadium trichloride with hydrogen on a heated tungsten wire. The aluminothermic process can be used on a fairly large scale, but the upper limit of purity of the brittle product is only about 98 percent. Carbon reduction of the oxide also yields a relatively impure, brittle product.

The reduction of vanadium pentoxide with calcium using iodine to obtain additional heat yields a regulus of ductile vanadium. The reduction is carried out in a high-fired magnesia-lined steel bomb. The typical charge in a 1½-liter crucible is 300 gm V_2O_5 , 552 gm calcium, and 150 gm iodine. Reductions yielding up to 1 kg of metal have been made. The yield is approximately 80 percent of theoretical. The ductility of the product depends not only on the relative amounts of calcium and iodine but also on the purity of the starting materials.

Powdered vanadium is obtained by the bomb reduction of vanadium trioxide with calcium. This powder is consolidated by compacting at 15 to 20 ton/sq in. and sintering at 2550° to 2750°F in a vacuum. The sintered product is ductile and can be fabricated by rolling.

Electro Metallurgical Co., a division of the Union Carbide and Carbon Corporation, has developed a process for the production of relatively large quantities of "ductile" vanadium but has not disclosed the method used for its production. This metal will be referred to as commercial "ductile" vanadium. The ductility of this commercial product is somewhat less than that of metal produced on an experimental basis by other processes. The lower ductility is probably the result of slightly higher oxygen content in the commercial product.

Typical analyses of metal produced by various methods are shown in Table 1.23.1.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants are shown in Table 1.23.2.

HEALTH HAZARDS

Vanadium compounds are toxic and must be handled with care to avoid inhalation or ingestion. Personnel who work with or may be exposed to vanadium and its compounds should have competent medical direction.

Table 1.23.1—Typical Analyses of Various Types of Ductile Vanadium

Method of reduction	Analysis, wt-%							
	V	C	Fe	Si	Ca	O	H	N
Calcium-reduced V_2O_5	99.6	0.23	<0.1	0.01	0.01	0.017 to .070	0.002	0.006 to .028
Thermal reduction of iodide	0.07	.002012	.005	.008
Calcium reduction of V_2O_5	99.7 to 99.8	.05	.0105	.1 to .2501 to .015
Commercial "ductile" vanadium	99.8 to 99.9	.03 to .0705 to .12	0.001 to .004	.02 to .04

Table 1.23.2—Physical and Chemical Constants of Vanadium

Thermal-neutron-absorption cross section, barns/atom	4.7 ± 0.2
Density, * gm/cm ³	
Theoretical	6.11
As reduced	6.11
As cold worked	6.17
Melting point, °C	1900 ± 25°C
Boiling point, °C	3400 (calculated)
Heat of fusion, kcal/mole	4.0
Heat of vaporization, kcal/mole	106
Specific heat, † cal/(gm)(°C)	
0°C	0.120
300°C	.127
900°C	.152
1300°C	.176
1600°C	.197
Vapor pressure, atm	
1867°C	10 ⁻⁵
2067°C	10 ⁻⁴
2277°C	10 ⁻³
2627°C	10 ⁻²
3527°C	1
Enthalpy (25°C), kcal/mole	1.26
Entropy (25°C), cal/(mole)(°C)	7.05
Specific resistance (20°C), μohm-cm	24.8
Coefficient of linear thermal expansion, per °C	
23°–100°C	8.3 × 10 ⁻⁶
23°–500°C	9.6 × 10 ⁻⁶
23°–900°C	10.4 × 10 ⁻⁶
23°–1100°C	10.9 × 10 ⁻⁶
Thermal conductivity, ‡ cal/(sec)(cm)(°C)	
100°C	0.074
500°C	.088
Crystal structure	Body-centered cubic
Lattice constants (a ₀), Å	
Calcium-reduced	3.0278
Iodide	3.0258
Allotropic transformations	None confirmed

*Gm/cm³ × 62.43 = lb/cu ft

†Cal/(gm)(°C) × 1 = Btu/(lb)(°F)

‡Cal/(sec)(cm)(°C) × (2.419 × 10³) = Btu/(hr)(ft)(°F)

MECHANICAL PROPERTIES

Since ductile vanadium has only recently become available in appreciable quantities, data on its mechanical properties are limited. The properties of the metal are sensitive to small quantities of impurities, and metal obtained by different reduction processes has widely varying properties. Oxygen, nitrogen, and hydrogen readily embrittle the metal when it is heated in contact with these gases at temperatures much in excess of 575°F. Oxygen, in particular, has a drastic effect on the mechanical properties, more than about 0.05 percent in solid solution rendering the metal difficult to cold work.

TENSILE AND COMPRESSION PROPERTIES

Table 1.23.3 shows the tensile properties of iodide, calcium-reduced, and commercial "ductile" vanadium. Iodide metal, which is the purest metal available, has a tensile strength of 31,600 lb/sq in. and a uniform elongation of 17 percent. The true-stress, true-strain curve for this metal is shown in Fig. 1.23.1. The true strain, δ , is defined as:

$$\delta = \ln \frac{L}{L_0} = \ln (e + 1)$$

where:

L = final length, L_0 = initial length, and e = nominal strain = $L - L_0/L_0$. The true stress, σ , is likewise defined as:

$$\sigma = \frac{P}{A} = \frac{P}{A_0} (e + 1)$$

where:

P = load on specimen in pounds, A = final area, and A_0 = initial area. The data of Fig. 1.23.1 can be used to predict the yield strength of the metal for any given amount of cold work. Figure 1.23.2 shows the calculated increase in yield strength produced by increasing amounts of cold work. The correlation of yield strength with Vickers hardness is shown in Fig. 1.23.3.

The tensile strength of commercial "ductile" vanadium is more than twice that of iodide metal, and the elongation is much less. The effect of cold work on the tensile properties of this metal is also shown.

The properties of calcium-reduced metal are intermediate between those of iodide metal and commercial "ductile" metal.

The modulus of elasticity of vanadium is relatively high, 20×10^6 lb/sq in., and the modulus-density ratios of steel and vanadium are practically equivalent, 3.7 million.

The dynamic shear modulus as determined by the ultrasonic-pulse technique is 6.74×10^6 lb/sq in. Young's modulus determined by this same method is 18.4×10^6 lb/sq in., and Poisson's ratio is 0.36.

No data are available on the effect of temperature on the tensile properties of vanadium.

HARDNESS

The hardness of vanadium from various sources is also indicated in Table 1.23.3. The work-hardening characteristics of iodide metal are shown in Fig. 1.23.4. The rate of work hardening is low and $\frac{1}{4}$ -in.-thick sheet can be cold rolled to 0.001-in.-thick foil without

Table 1.23.3 — Mechanical Properties of Vanadium

Reduction method	Fabrication history	Proportional limit, lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Ultimate strength, lb/sq in.	Elongation, %	Reduction of area, %	Hardness	Modulus of elasticity, 10^6 lb/sq in.
Calcium-reduced V_2O_5	As extruded and cold straightened	...	58,000	63,000	35	64	165 VHN	19.9
Calcium-reduced V_2O_5	Extruded at 1800°F, annealed	...	36,000	54,000	25 to 35	25 to 50	...	19
	Cold-rolled 99%	...	88,000	94,000	0.5 to 1.5
Iodide	Arc melted, cold-rolled 90%, annealed 1 hr at 1475°F	12,200	16,700	31,600	17*	75	64 VHN	20.1
Calcium-reduced V_2O_5 (powder process)	Annealed	100,000	23	...	230 VHN	...
	Work hardened	140,000	3	...	330 VHN	...
Commercial "ductile" (process unknown)	Hot worked and annealed 1 hr at 1500°F	61,000	76,000	81,000	7	...	76 R B	21.5
Commercial "ductile" (process unknown)	Cold-rolled 60%	63,000	101,000	107,000	1 to 2.5	...	92 R B	...
Commercial "ductile" (process unknown)	Cold-rolled 75%	68,000	110,000	117,000	1 to 2.5	...	95 R B	...
Commercial "ductile" (process unknown)	Cold-rolled 80%	69,000	142,000	155,000	1 to 2.5	...	29 R C	...

* Broke outside gage marks

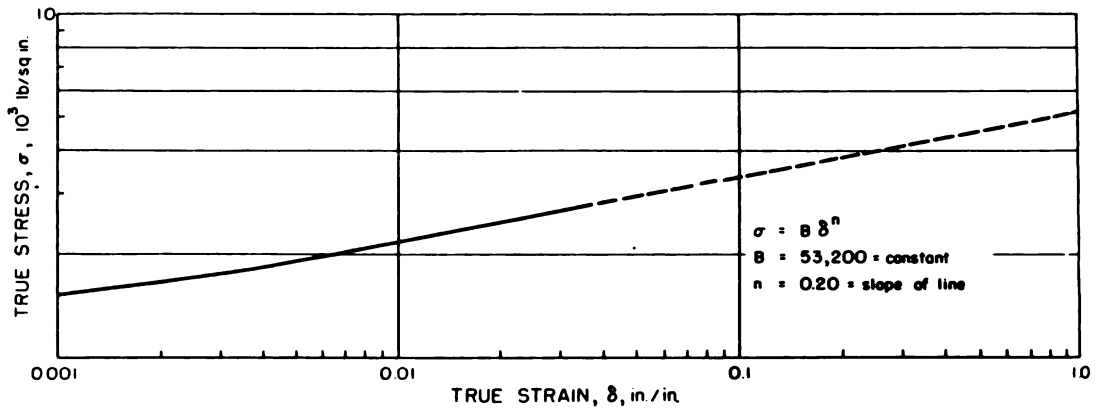


Fig. 1.23.1 — True Stress-True Strain for Iodide Vanadium. Submitted by Battelle Memorial Institute, Aug. 20, 1952.

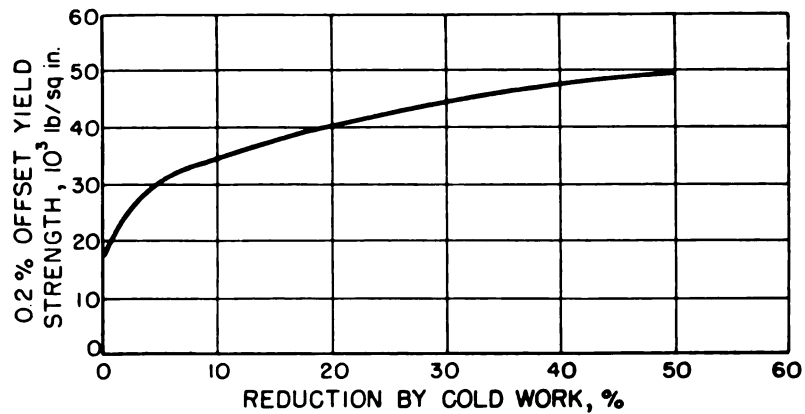


Fig. 1.23.2 — Effect of Cold Work on the Yield Strength of Iodide Vanadium as Predicted From True Stress-strain Data. Submitted by Battelle Memorial Institute, Aug. 20, 1952.

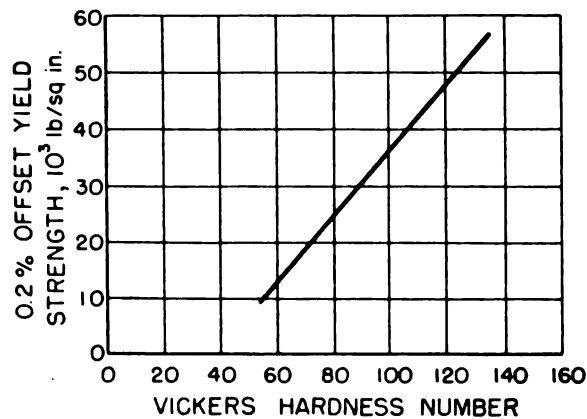


Fig. 1.23.3 — Correlation of Vickers Hardness and Yield Strength for Cold-worked Iodide Vanadium. Submitted by Battelle Memorial Institute, Aug. 20, 1952.

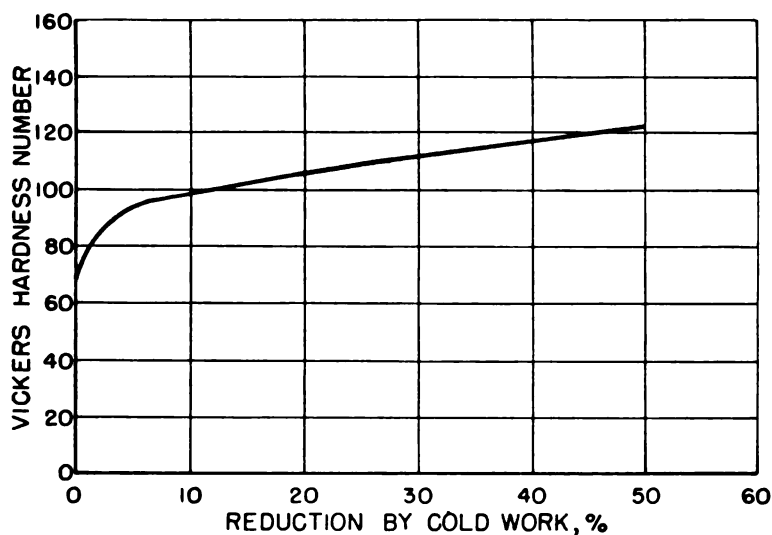


Fig. 1.23.4—Effect of Cold Work on the Hardness of Annealed Iodide Vanadium. Submitted by Battelle Memorial Institute, Aug. 20, 1952.

intermediate anneals. Figure 1.23.5 shows the effect of oxygen on the hardness of calcium-reduced metal.

CREEP

Few data on the creep properties of vanadium are available. Preliminary survey-type stress-to-rupture tests on extruded calcium-reduced metal have been made at 1000°F. In these tests, one bar failed on loading to 23,100 lb/sq in. A second bar stressed at 18,000 lb/sq in. failed in 60 hr and 7 percent elongation. This bar, however, had a defect in the reduced section which probably affected the results. The third bar withstood 1100 hr at 16,000 lb/sq in. without failure. After 1100 hr, the load on this sample bar was increased daily. The bar failed at 28,000 lb/sq in. after 200 additional hours with a total elongation of 15 percent.

MELTING AND CASTING

A satisfactory refractory to contain molten vanadium has not been found. Induction melts in vacuum in ThO_2 , BeO , ZrO_2 , Al_2O_3 , and MgO crucibles show a marked increase in hardness and a loss of ductility. Cerium sulfide is the only crucible material which does not adversely affect the hardness of the melt, but vanadium melted in cerium sulfide picks up sulfur which is observed as an intergranular precipitate in the metal. Table 1.23.4 shows the analyses of induction melts made in various crucible materials.

Vanadium is melted most successfully by the arc-melting process in water-cooled copper crucibles. This process is essentially the same as that used for other reactive metals, such as zirconium, titanium, and molybdenum. A tungsten electrode is used, and an inert atmosphere, either argon or helium, is maintained during the melting operation. There is little increase in hardness during arc melting, but a coarse-grained ingot results. Arc-melted buttons of iodide vanadium tend to crack intergranularly on cold rolling, and hot working may be required to refine the grain size.

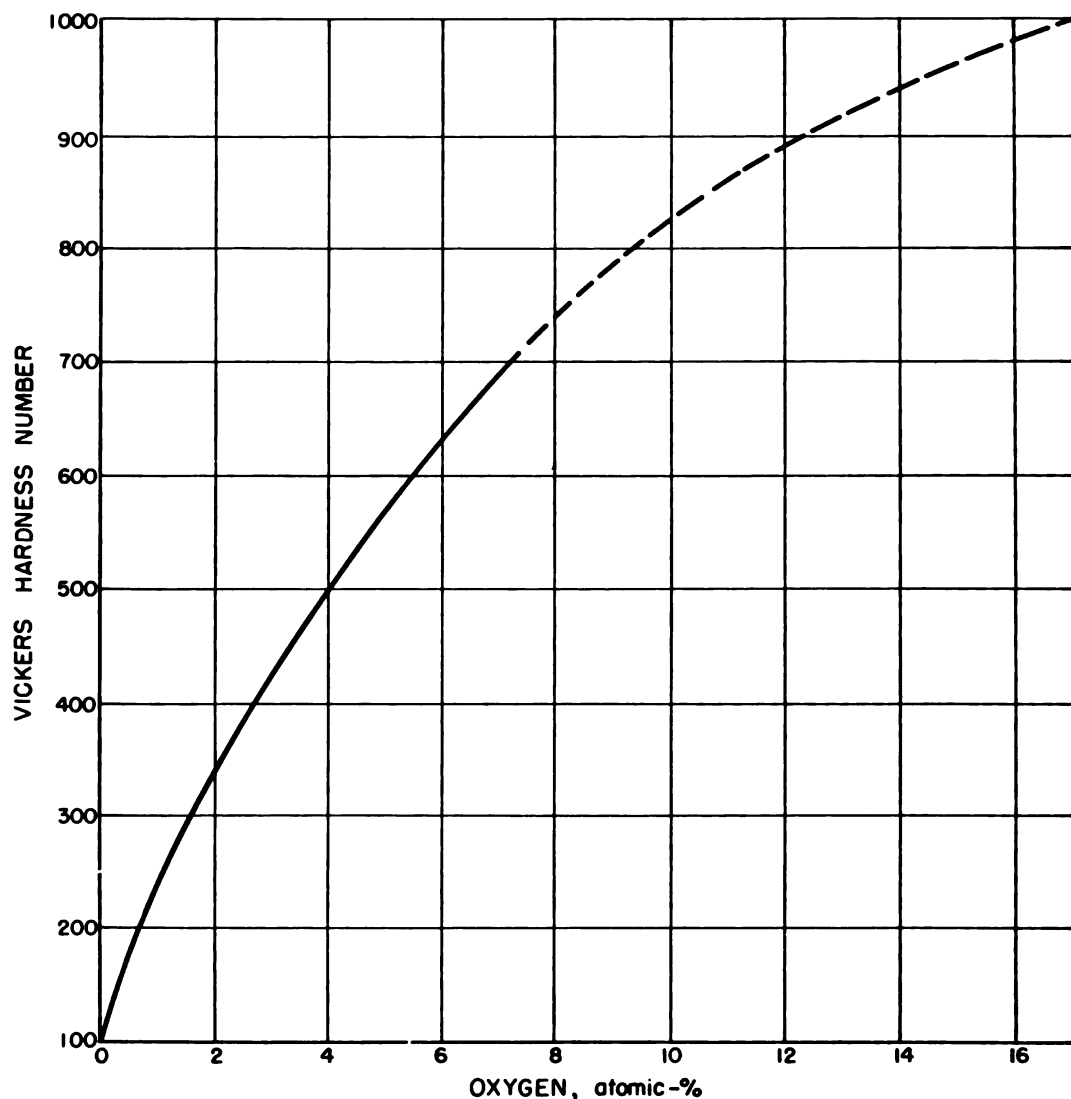


Fig. 1.23.5—Vickers Hardness of Calcium-reduced Vanadium as a Function of Oxygen Content. Based on data of A. U. Seybolt.

Table 1.23.4—Analyses of Induction Melts* Made in Various Crucible Materials

Crucible material	Analysis, wt-%												VHN after melting†
	O	H	N	Fe	Al	Si	Ca	Be	Zr	Cu	Ce	S	
CaO	1.13	0.001	0.13	0.01	<0.005	0.05	0.005	0.005	<0.05	545
Al ₂ O ₃	1.52	.008	.20	.01	.80	.03	.005	<.001	<.05	569
BeO	1.15	.006	.21	.01	.15	.07	.005	.02	<.05	564
CeS	0.04	.003	<.04	.0302	.005	0.005	0.03	0.15	182
Arc Melt	.05	.012	<.04	.0302	.005001	<.01	...	211

* Melting stock was calcium-reduced metal with the following analysis: oxygen, 0.055 wt-%; hydrogen, 0.0032 wt-%; nitrogen, 0.0120 wt-%; and carbon, 0.15 wt-%

† Initial hardness, 205 Vickers

FORMING AND FABRICATION

Pure vanadium is a soft, ductile metal which does not work harden rapidly. The metal can be fabricated by most metalworking processes but must be protected from contact with gases during hot-working operations. Sheet, rod, wire, and tubing have been made.

ROLLING

For hot rolling commercial "ductile" metal, the ingot is sheathed in a stainless steel jacket. This jacket is generally about $\frac{1}{8}$ in. thick and is welded so that a gas-tight, close-fitting box is provided around the ingot.

The optimum breakdown temperature is 2000° to 2100°F. Once the cast structure is broken up, the hot-working temperature may be reduced to 1475° to 2100°F. The finishing temperature is usually 1100° to 1300°F, but rolling can be continued down to room temperature without appreciable work hardening. After rolling, the steel sheath is removed and the surface of the vanadium scalped to remove surface contamination by the steel jacket.

The rolling practice with respect to passes and reduction follows that established for austenitic stainless steels. In rolling sheet, the ingot is hot rolled to about $\frac{1}{4}$ in. thick, scalped, and annealed 1 hr at 1650°F. The strip is then finished to the desired size by cold rolling. Total reductions of 85 percent or more, depending on the quality of the metal and the section involved, can be made without edge cracking. The cold-rolling characteristics are improved by working at 400° to 600°F.

In the fully annealed or hot-rolled state, sections $\frac{1}{4}$ in. or greater in thickness are relatively brittle. The metal can be cold rolled, however, and after cold rolling the apparent brittleness disappears. This phenomenon, as yet unexplained, may be related to the increased malleability on heating from room temperature to 575°F.

Calcium-reduced metal can be cold rolled to reductions in excess of 99 percent without intermediate anneals, and iodide metal has similar ductility.

SWAGING

Vanadium can be swaged at room temperature in dies designed for mild steel.

DRAWING

Small-diameter tubing can be drawn from calcium-reduced metal, and fine wire also has been made. The metal has some tendency to seize to the dies, and special lubricants are required.

EXTRUSION

The extrusion of vanadium is feasible, and this process has been used to consolidate calcium-reduced metal into rod. The reduced metal is cold rolled to sheet roughly 0.100 in. thick and is then cut into small pieces. These pieces are packed in a mild-steel can having $\frac{1}{16}$ - to $\frac{1}{8}$ -in.-thick walls. The can is evacuated and welded shut. This billet is heated to 2000°F and extruded to rod or tubing. The extrusion of a $\frac{3}{4}$ -in.-diameter rod from a 2-in.-diameter can required 295 tons load. The extruded rod has an average hardness of 165 Vickers and a fine, recrystallized grain size.

FORGING

Large sections may be heated briefly in air and forged in open dies. Considerable scaling occurs, and the surface layers must be scalped to remove the contaminated metal.

No data are available on the rate of penetration of oxygen and nitrogen, but there is some evidence that the diffusion rate of oxygen is high.

Sheath forging is unsatisfactory because of sheath cracking and resulting contamination of the metal by the atmosphere.

POWDER METALLURGY

Vanadium powder produced by the reduction of V_2O_5 with calcium is compacted at 15 to 20 tons/sq in. The compacts are sintered in vacuum for 1 to 2 hr at 2550° to 2750°F. The properties of the resulting metal are shown in Table 1.23.3.

Vanadium-uranium alloys containing up to 40 weight-percent (12.5 atomic-percent) uranium have been made by powder-metallurgy processes. The vanadium powder was obtained from calcium-reduced metal by heating in hydrogen at 1100°F, slow cooling to 750°F, and soaking at this temperature overnight. The embrittled metal, after furnace cooling, was crushed and the hydrogen removed by heating in vacuum at temperatures above 1100°F. The compacts were pressed at about 50 tons/sq in. and sintered at temperatures up to 2370°F.

JOINING

Vanadium may be welded by the Heliarc process with argon shielding. Good shielding is necessary and best results are obtained in a "dry" box or enclosed box filled with the inert atmosphere. The metal has smooth welding characteristics, and annealing after welding is unnecessary. The dimensional stability of welded joints is improved by stress relieving at about 1100°F in an inert atmosphere. No data are available on other methods of joining vanadium.

MACHINING

The machinability of pure vanadium is about equivalent to that of cold-rolled steel. The metal is free cutting, and tools such as those used for copper with a high rake angle of about 15° and a clearance angle of 7° to 15° are used. To produce a good surface finish, high cutting speeds and light cuts are employed; a light lubricant also improves the surface finish. Vanadium is easier to machine than Monel, nickel, stainless steel, and titanium but more difficult than copper, aluminum, or yellow brass.

HEAT TREATMENT

Figure 1.23.6 shows the effect of annealing temperature on the hardness and grain size of cold-worked iodide metal. The softening of cold-worked calcium-reduced metal is also shown.

The recrystallization temperature is between 1100° to 1300°F. Vacuum annealing or annealing in a noble-gas atmosphere is required to prevent contamination by the atmosphere. Vacuum annealing is preferable because it is occasionally necessary to pump out hydrogen. The usual annealing treatment is 1 hr at 1500° to 1650°F.

CORROSION BEHAVIOR

CORROSION IN AIR

Like niobium and tantalum, vanadium is very susceptible to embrittlement by atmospheric gases. Oxygen, nitrogen, and hydrogen readily embrittle the metal when it is

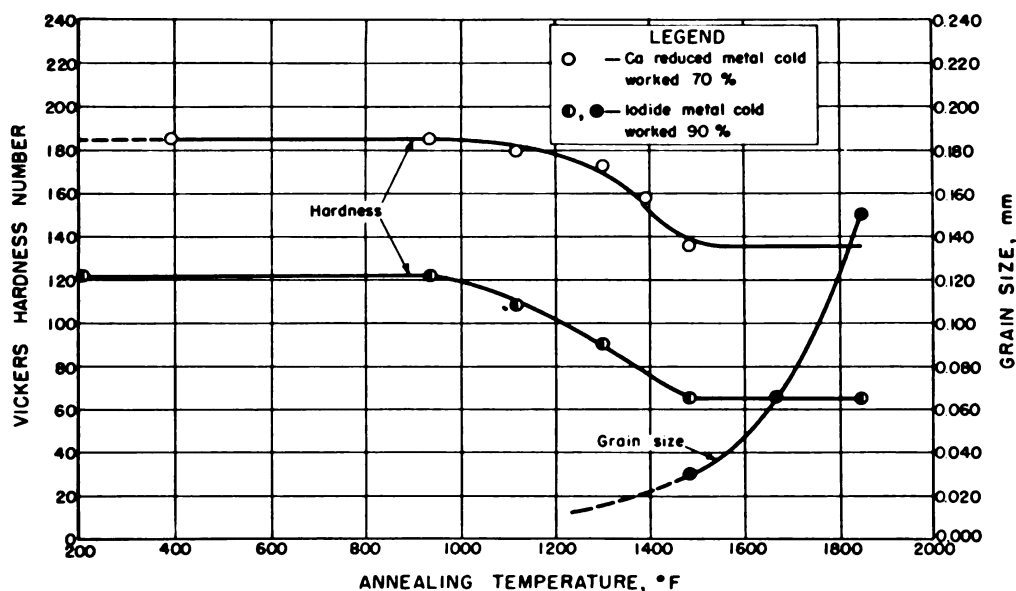


Fig. 1.23.6—The Effect of Annealing Temperature on the Hardness and Grain Size of Vanadium. Curve for iodide vanadium submitted by Battelle Memorial Institute; curve for calcium-reduced metal based on data supplied by A. U. Seybolt.

heated in contact with these gases at temperatures above 575°F. Little reaction occurs below this temperature, but a pronounced decrease in scaling resistance occurs between 1100° and 1300°F. This change is associated with the formation of V_2O_5 , which melts at 1035°F. Table 1.23.5 shows the effect of various binary-alloy additions on the short-time scaling resistance of vanadium at 1380°F.

CORROSION IN LIQUID METAL

Few data on the corrosion resistance of pure vanadium in liquid metals are available. Table 1.23.6 summarizes the available data on liquid-metal corrosion and indicates that vanadium has considerable promise as a container material.

CORROSION IN ACID AND OTHER MEDIA

Vanadium is reported to be fairly resistant to hydrochloric acid but is attacked rapidly by nitric acid. The commercial "ductile" vanadium is resistant to pitting and corrosion by sea water and salt spray.

Calcium-reduced metal immersed 5 hr at 203°F lost 1.4 weight-percent in 3N hydrochloric acid and 12 weight-percent in 12N acid. After a 60-hr exposure at 74°F, the metal showed no weight loss in 3N acid and 1.5 weight-percent loss in 12N acid.

METALLOGRAPHY

The mechanical polishing of vanadium for metallographic examination is similar to that of other soft metals. The sample may be ground on wet or dry paper through 600 grit and polished on airplane-wing cloth using Precisionite coarse abrasive No. 87725. Final

Table 1.23.5 — Short-time* Oxidation Tests of Vanadium-base Alloys at 1380°F in Air
(Exploration of Vanadium-Base Alloys, Report No. 3, Armour Research Foundation)

Alloy content, wt-%	Weight decrease, mg/cm ²		
	Apparent†	True‡	Penetration, cm/hr
5 beryllium	80.4	111	0.0182
7.5 carbon	138.0	145	.0237
10 aluminum	3.5	33.1	.0054
10 titanium	55.0	87.6	.0143
15 titanium	27.4	75.6	.0123
25 titanium	1.8	62	.0102
35 titanium	13.3§	37.2	.0061
45 titanium	45.4§	96.1	.0157
65 titanium	68.7	79.1	.0129
85 titanium	4.7	29.9	.0049
10 chromium	30.6	47.2	.0077
10 manganese	179.0	185	.0302
10 iron	93.0	111	.0182
10 iron	106.0	113	.0185
10 cobalt	138.0	147	.0241
10 nickel	39.6	68.5	.0112
10 niobium	110.0	123	.0201
7.5 molybdenum	181.0	184	.0301
10 tin	119.0	144	.0236
10 tantalum	133.0	143	.0234
None	211.0	¶	.0345
None	221.0	¶	.0361

*Testing time = 1 hr at temperature

†Without removing scale

‡After mechanically removing scale

§This sample showed an apparent weight increase

¶Scale could not be satisfactorily removed and probably contributes a negligible error

Table 1.23.6 — Corrosion of Vanadium in Liquid Metals

Liquid metal	Test temperature, °F	Remarks
Sodium	932	Good resistance; corrosion rate 0.2 mg/(cm ²)(mo)
55.5 Bi, 44.5 Pb	1200	Good resistance, static test, 500 hr
52 Bi, 32 Pb, 16 Sn	1200	Good resistance, static test, 500 hr
52.3 Bi, 21.9 In, 25.8 Pb	1200	Good resistance, static test, 500 hr
49.5 Bi, 21.3 In, 17.6 Pb, 11.6 Sn	1200	Good resistance, static test, 500 hr
57.5 Bi, 25.2 In, 17.3 Sn	1200	Good resistance, static test, 500 hr
55.5 Bi, 44.5 Pb	900	Dynamic test, 1008 hr; sample gained weight; generally good resistance
52 Bi, 32 Pb, 16 Sn	1200	Dynamic test, 1008 hr; 20 mg/(cm ²)(mo) attack

polishing is accomplished on airplane-wing cloth with Precisionite fine abrasive No. 87724. Etching to bring out the structure may be done chemically in 1 part HF, 1 part HNO₃, 2 parts H₂O or electrolytically in 10-percent HCl at room temperature and 3-6 volts.

VANADIUM ALLOYS

With the exception of the vanadium-uranium, vanadium-titanium, and the vanadium-iron systems, vanadium-rich alloys have not been studied extensively. A research program directed towards increasing the knowledge of the properties of vanadium-base alloys is being sponsored by the Air Force at Armour Research Foundation, and some work is in progress at Iowa State College. With the increasing availability of commercial "ductile" vanadium, interest in vanadium-base alloys will undoubtedly increase, and additional information will become available.

The constitutional diagrams of vanadium with uranium and iron are shown in Figs. 1.23.7 and 1.23.8. The uranium-rich vanadium alloys have good fabricating characteristics, and alloys up to 15 atomic-percent vanadium have been hot rolled at 1100°F. Table 1.23.7 summarizes the available information on the alloy behavior of vanadium with 20 elements. Tentative phase diagrams based on the limited information available are shown in Figs. 1.23.9 through 1.23.16. A comparison of the annealed hardness of vanadium-base alloys is shown in Fig. 1.23.17.

Vanadium appears to be an effective solvent metal for most metallic elements, and the possibilities for alloy development are broad.

The oxygen-vanadium system is of considerable importance because of the embrittling effect of exceedingly small quantities of this element. Solubility studies indicate that several atom-percent of oxygen are interstitially soluble in the body-centered cubic structure. Further addition of oxygen results in a two-phase region of a body-centered tetragonal phase and the cubic phase. This region persists to about 15 atom-percent at which composition the structure is completely body-centered tetragonal. The body-centered tetragonal phase has a homogeneity range of only a few atom-percent; and with further additions of oxygen, vanadium oxide appears in the structure.

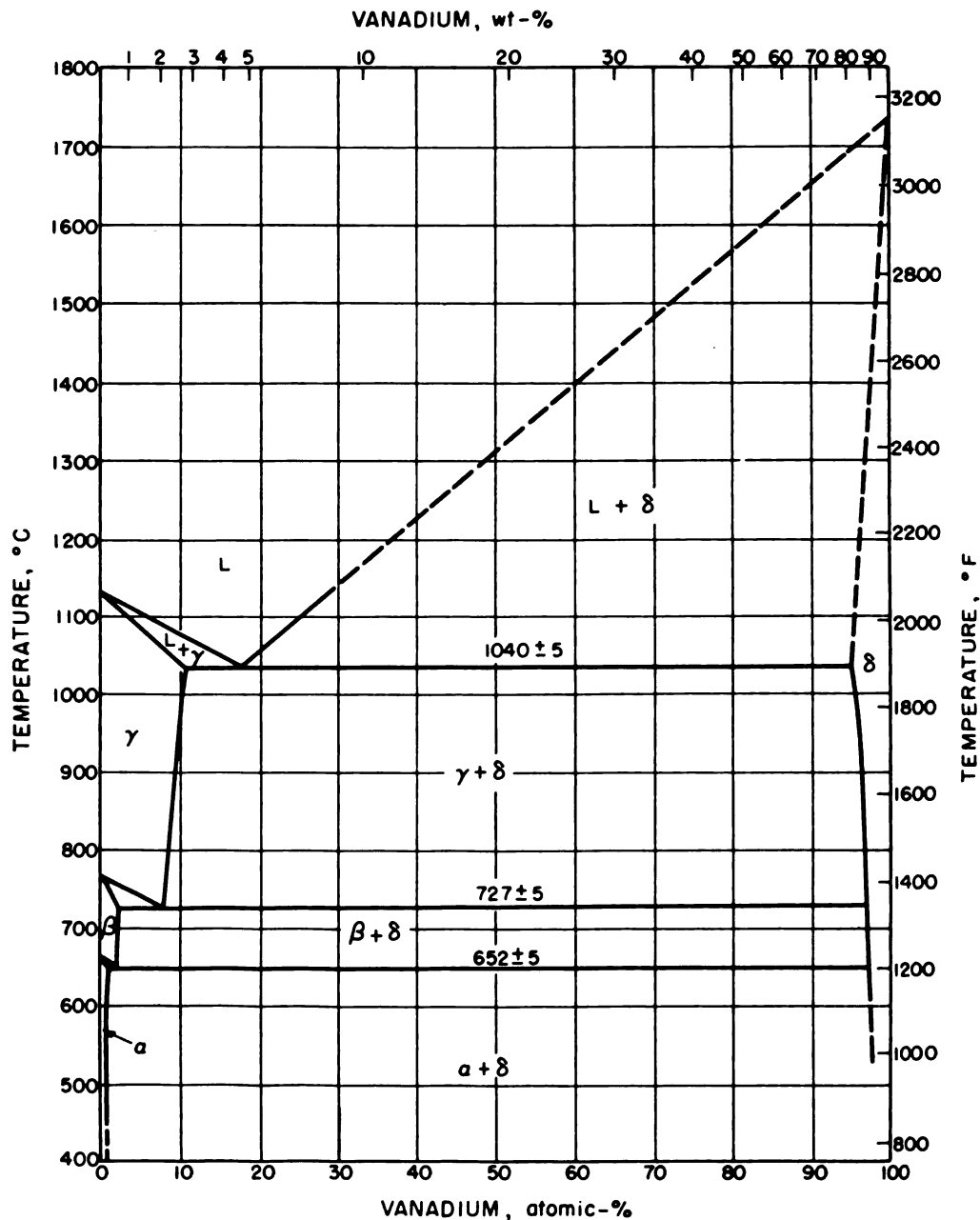


Fig. 1.23.7—The Uranium-Vanadium Constitutional Diagram. Reprinted from The Vanadium-Uranium Constitutional Diagram, H. A. Saller and F. A. Rough, BMI-716, Dec. 15, 1951.

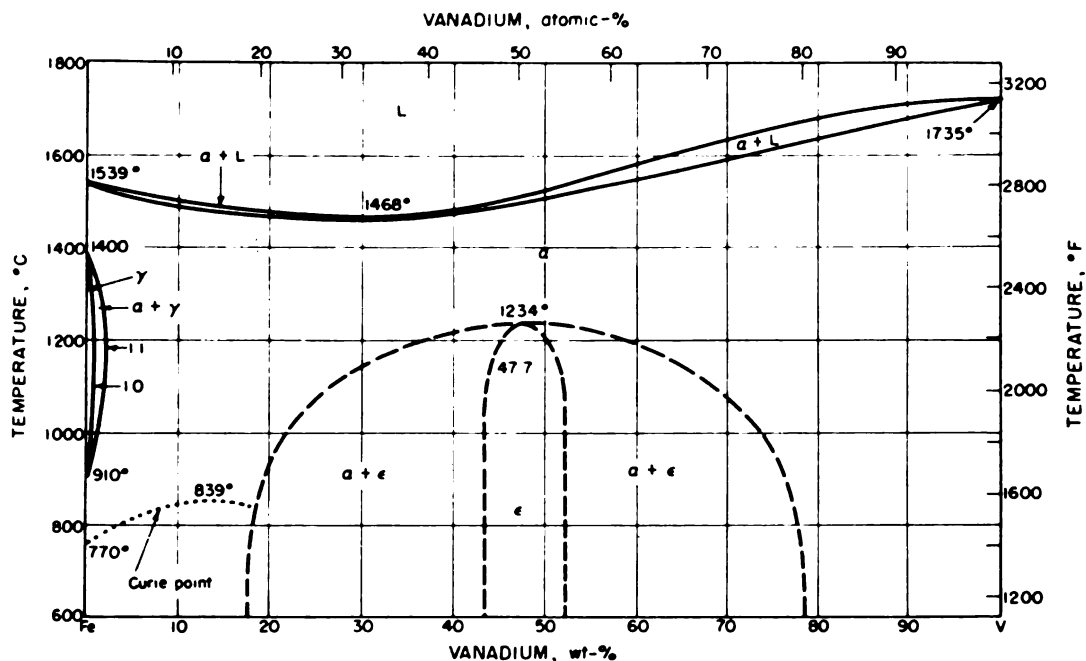


Fig. 1.23.8—The Constitutional Diagram of the System Iron-Vanadium. Reprinted from ASM Metals Handbook, 1948 Edition.

Table 1.23.7—Summary of Information on Alloying Behavior of Vanadium
(Exploration of Vanadium Base Alloys, Report No. 4, Armour Research Foundation)

Solute element	Solubility limit, wt-%	Reaction between primary solid solution and first intermediate phase	Intermediate phases
Be	< 1	Eutectic at ~15 wt-% Be	VBe ₂
B	< 0.25	Eutectic	VB
C	< 1	Eutectic at ~3.5 wt-% C	V ₃ C, VC
N*	VN
O	VO, V ₂ O ₅ , V ₂ O ₆ , VO ₃
Al	~35	Peritectic ~1370°C	VAl ₃
Si	~4.5	Eutectic ~8 wt-% Si	V ₃ Si
Ti	100
Cr	> 40
Mn	> 10	...	Sigma phase (77% Mn)
Fe	> 10	...	Sigma phase (50% Fe)
Ni	~60	Eutectic at ~70 wt-% Ni	Sigma phase, orthorhombic structure
Cu	~9	Monotectic	...
Nb	> 10
Mo	~30
Ag	0
Sn	> 10
Ta	< 80	...	Sigma phase, orthorhombic structure

*See also Hahn Zeit. Anorg. Chemie 258, 58, 1949

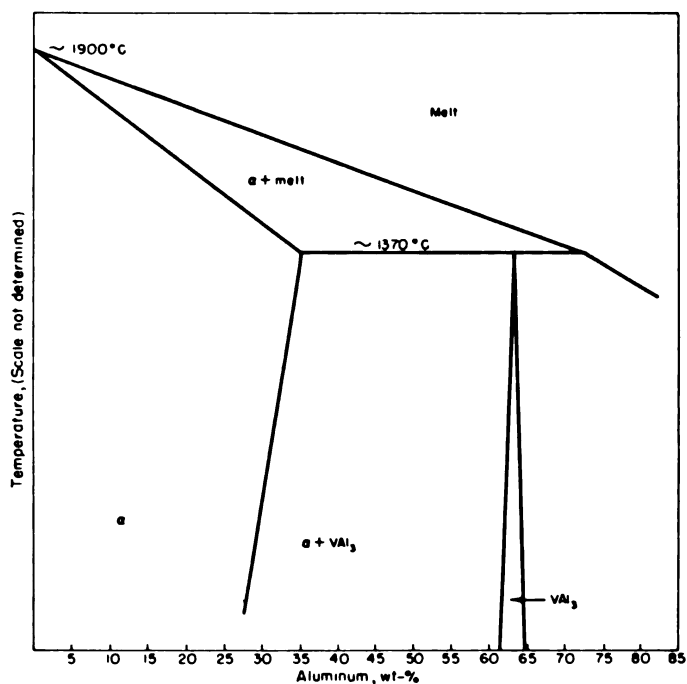


Fig. 1.23.9—Tentative Summary of Phase Relationships in the Vanadium-Aluminum System. Based on data of Armour Research Foundation.

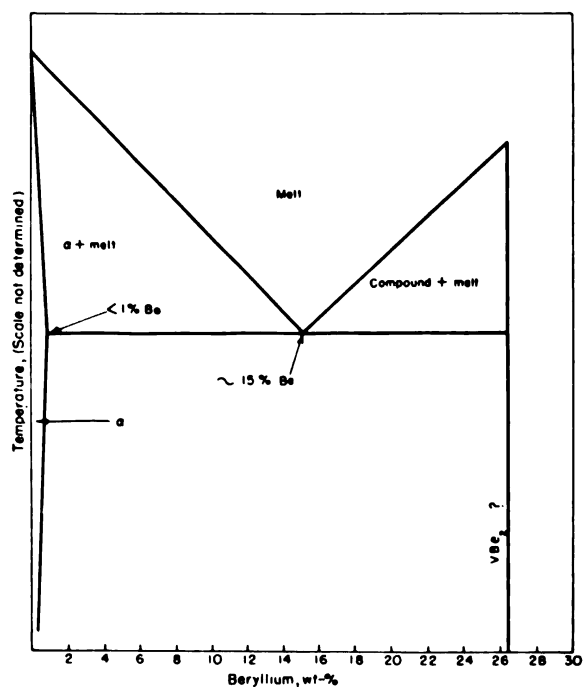


Fig. 1.23.10—Tentative Summary of Phase Relationships in the Vanadium-Beryllium System. Based on data of Armour Research Foundation.

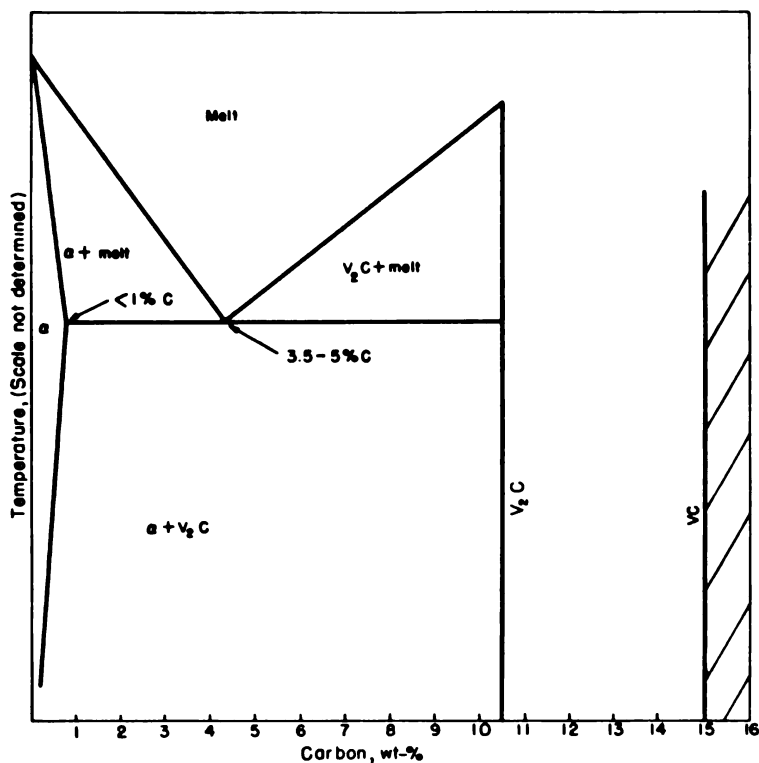


Fig. 1.23.11 —Tentative Summary of Phase Relationships in the Vanadium-Carbon System. Based on data of Armour Research Foundation.

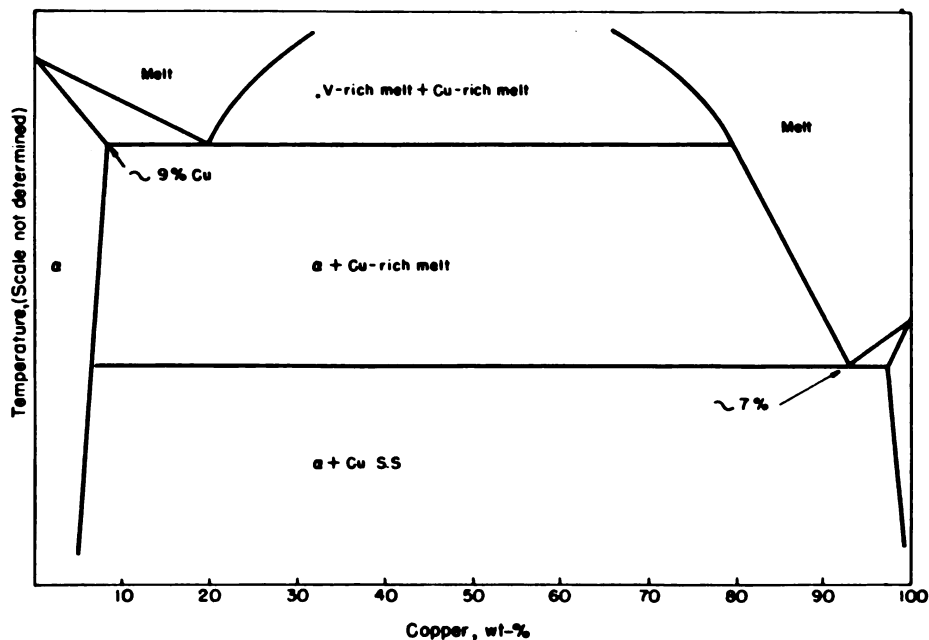


Fig. 1.23.12 —Tentative Summary of Phase Relationships in the Vanadium-Copper System. Based on data of Armour Research Foundation.

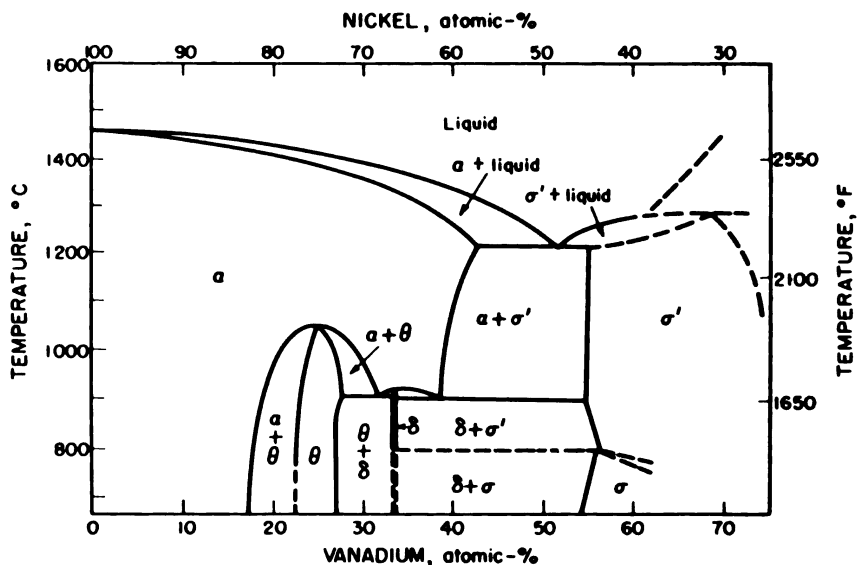


Fig. 1.23.13—Constitutional Diagram of the System Nickel-Vanadium. Reprinted from W. B. Pearson and W. Hume-Rothery, *The Constitution and Structure of Nickel-Vanadium Alloys in the Region 0-60 Atomic Percent Vanadium*, *Journal of the Institute of Metals*, Aug. 1952.

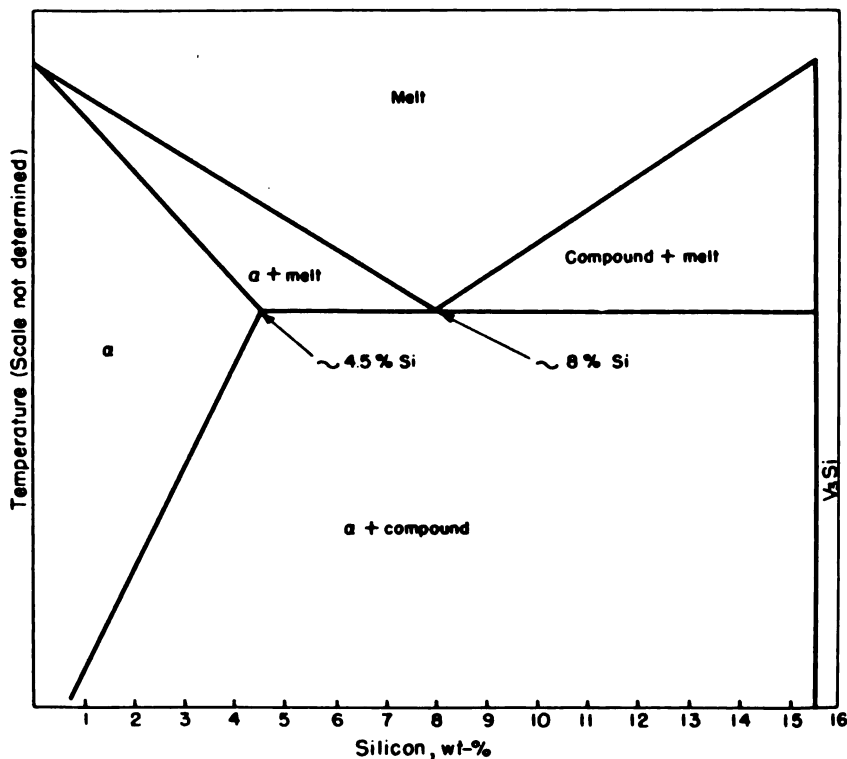


Fig. 1.23.14—Tentative Summary of Phase Relationships in the Vanadium-Silicon System. Based on data of Armour Research Foundation.

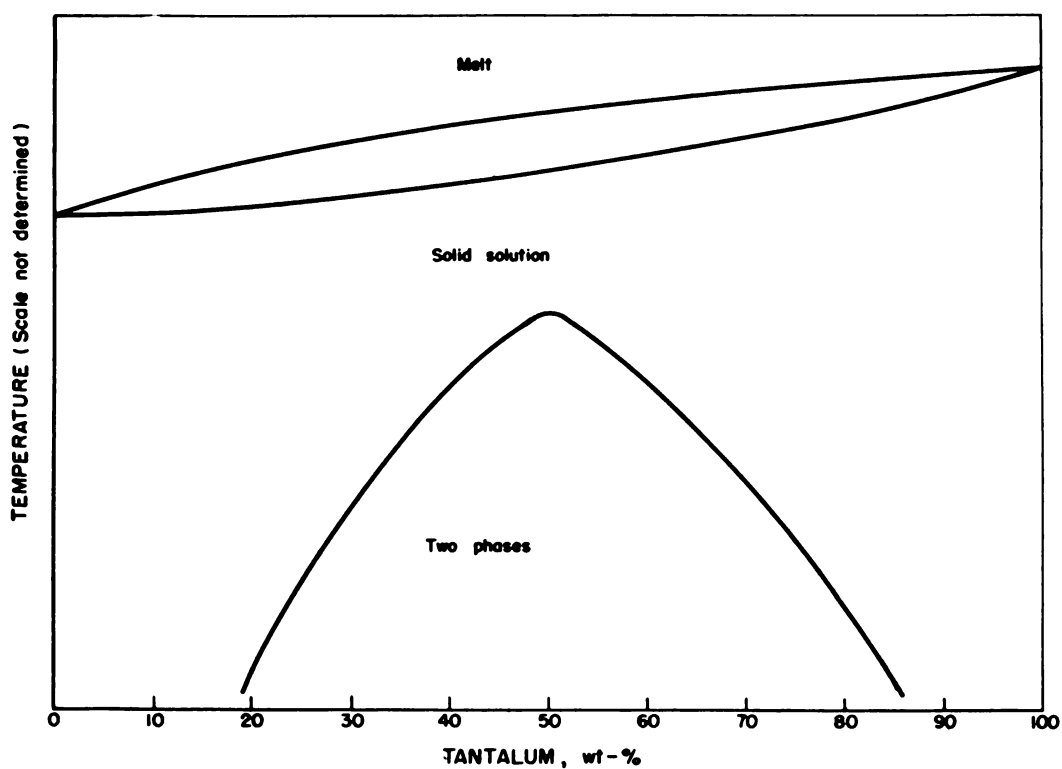


Fig. 1.23.15—Tentative Summary of Phase Relationships in the Vanadium-Tantalum System. Based on data of Armour Research Foundation.

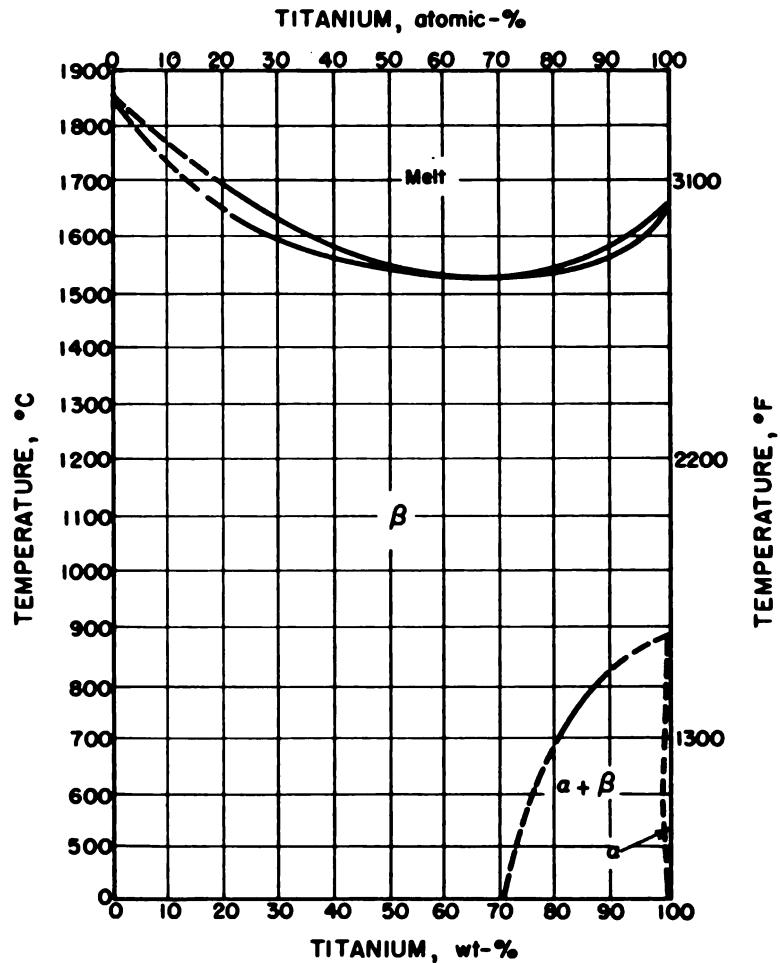


Fig. 1.23.16—The Constitutional Diagram of the System Titanium-Vanadium. Reprinted from Semi-annual Progress Report on Metallurgy, for the period April 1, 1951–September 30, 1951, H. A. Wilhelm, ISC-203, Mar. 31, 1952.

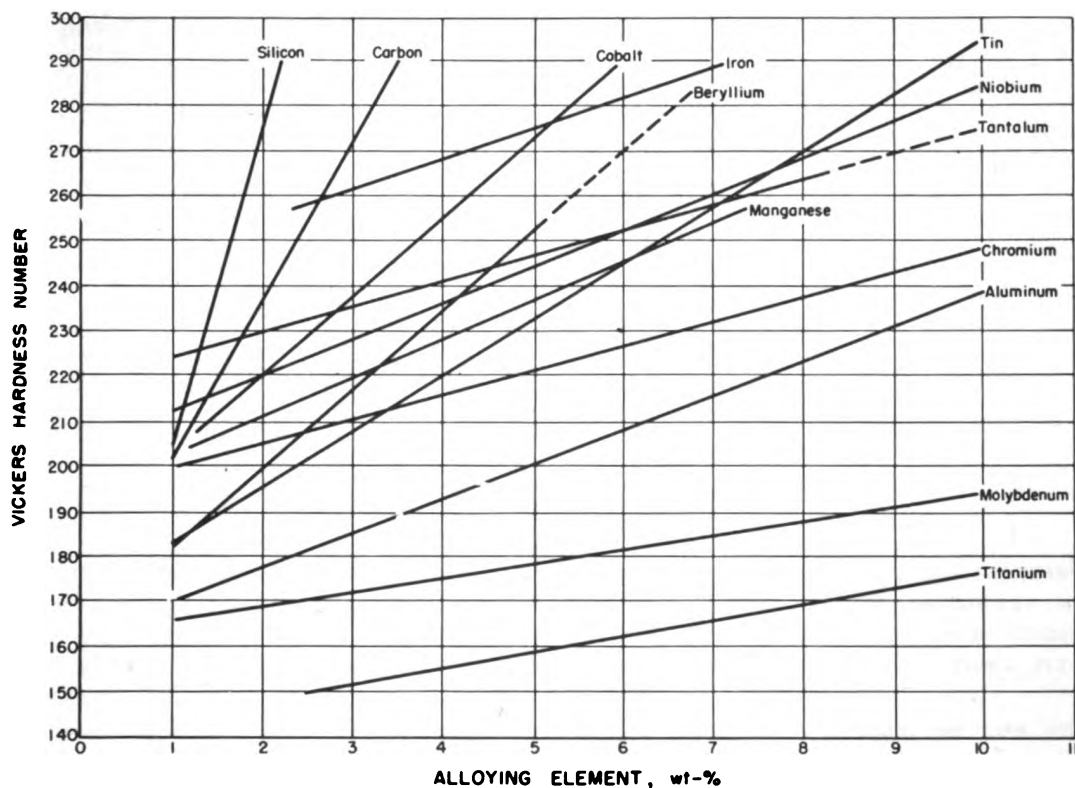


Fig. 1.23.17—Comparison of Annealed Hardness of Vanadium-base Alloys. Based on data of Armour Research Foundation.

SELECTED READING LIST

THE PREPARATION AND PROPERTIES OF IODIDE VANADIUM, J. W. Nash, H. R. Ogden, R. E. Durtch, and I. E. Campbell. Paper presented at May, 1952 Meeting of Electrochemical Society.

EXPLORATION OF VANADIUM-BASE ALLOYS, Reports 1 to 4, Armour Research Foundation, Air Force Contract No. AF 33(038)-8517, June 10, 1951, to January 10, 1952.

VANADIUM AS A POSSIBLE STRUCTURAL METAL IN NUCLEAR REACTORS, A. U. Seybolt, *J. Met. and Cer.*, p 23, January, 1951.

PRODUCTION OF DUCTILE VANADIUM BY CALCIUM REDUCTION OF VANADIUM TRIOXIDE, E. D. Gregory, W. C. Lilliendahl, and D. M. Wroughton, *J. Electrochem. Soc.* 98:395 (1951).

THE PREPARATION OF DUCTILE VANADIUM BY CALCIUM REDUCTION, R. K. McKechnie and A. U. Seybolt, *J. Electrochem. Soc.* 97:311 (October, 1950).

VANADIUM METAL—A NEW ARTICLE OF COMMERCE, A. B. Kinzel, *Metal Progress*, 58:315 (September, 1950).

VANADIUM AND ITS ALLOYS, W. B. Pearson, *J. Iron and Steel Inst.*, London, 165:149 (1950).

CHAPTER 1.24

Zirconium and Its Alloys

R. W. Dayton

REACTOR APPLICATION

Zirconium and its alloys are extremely important in the reactor development program of the Atomic Energy Commission. Although the virtues of zirconium for reactor use have been apparent in only the last five years, this material has been used in the construction of the first core of the submarine thermal reactor (STR). Because of its many virtues, zirconium must be given serious consideration for any future reactors.

The major advantages of zirconium are its low cross section for thermal neutrons, excellent corrosion resistance in many fluids, good mechanical properties, and good fabrication qualities. Some of these properties can be improved further by alloying.

The property of zirconium of compelling interest for reactor applications, its low cross section for thermal neutrons, was not always appreciated. This fact had escaped notice because even the purest naturally occurring ores of zirconium contain from $\frac{1}{2}$ to 3 weight-percent of hafnium, which has a high cross section and is retained with zirconium in all normal processing operations, owing to its chemical similarity.

When it was found that pure zirconium had a low cross section, intensive study was begun with the aim of using this material in the core of the STR. The progress which has been made in the technology of zirconium since that time has been so rapid that, in the intervening four or five years, hafnium separation processes have been developed and put into production, refining facilities have been expanded greatly, and the processing techniques and basic metallurgy of the material have been worked out. Work in the field has been so intensive that more is known now about zirconium than about some more common materials. In one characteristic, resistance to radiation damage, there are few materials about which more is known. Using the technology which has been developed, the first core for the STR now has been built.

Zirconium alloys have so many desirable properties that they would probably be used in all reactors in which a low thermal-neutron cross section is desirable, if it were not for certain limitations. The most serious of these are loss of strength and loss of corrosion resistance at high temperatures.

Currently, it is possible to use zirconium for thousands of hours in water at 600°F, with only superficial corrosion. It can be expected that the allowable temperature will be increased as improved materials are developed, and ultimate operation at 700°F for thousands of hours seems probable.

Some alloys tested in 1500 psi, 900°F steam corroded to a depth of only 0.3 mils in 400 hr. Short-time operation at such temperatures therefore appears possible now, with the prospect of further improvement.

In other media, temperature limitations are less clearly defined. In air, zirconium is probably usable at temperatures up to 900°F. It resists attack by some molten metals well, even to temperatures over 1500°F. In certain molten salts of current interest, temperatures a little over 1000°F are probably practical.

Protection against corrosion by coating zirconium with more corrosion-resistant metals is not promising. Weak, brittle layers of intermetallic compounds form at 1200°-1400°F between zirconium and those metals which have better corrosion resistance than zirconium alloys.

Zirconium loses strength rapidly at elevated temperatures. The strongest alloy yet tested at 930°F creeps at a rate of 10^{-4} percent/hr at a stress of only 4000 lb/sq in. Work in this field is continuing, and stronger alloys will probably be developed.

A considerable amount of work is in progress to improve the strength and corrosion resistance of zirconium alloys at high temperatures. However, the development of zirconium alloys with properties like those of stainless steels at temperatures over 1000°F appears unlikely. If such alloys were possible, it would be expected that promising leads would have been uncovered in the very extensive exploratory studies of the Bureau of Mines.

Until recently, most zirconium experience has been obtained with the unalloyed material. However, considerable attention is being given now to alloying to improve one or another of the properties of the base material. This work is in an early stage, and extensive data are available for only a few alloys. Thus, it is not yet clear what alloys will ultimately be important, and in this discussion, it will be necessary to make the best possible guess as to the future importance of specific alloys.

Materials which are expected to be of interest are described below in general terms.

CRYSTAL-BAR ZIRCONIUM

Zirconium of the highest purity is obtained by refining sponge by the de Boer iodide process. The material produced, called "crystal-bar" zirconium, is low in all impurities, especially in nonmetallic ones. For that reason, it is very ductile and easily worked. The major disadvantage of this material, aside from its lack of strength, is the sensitivity of its corrosion properties to the presence of small amounts of certain impurities. For example, material containing as little as 50 ppm of nitrogen is noticeably less corrosion resistant in water at 600°F than material containing 10 or 20 ppm of nitrogen. Since zirconium is avid for nitrogen, great care in avoiding contamination is required in all processing operations.

SPONGE ZIRCONIUM

Essentially all zirconium is now reduced from the chloride by magnesium using the Kroll process. When the starting material is pure, the sponge zirconium which is produced is also quite pure. The most important differences in purity between sponge and crystal-bar zirconium are the considerably higher oxygen content and the slightly higher nitrogen content of the sponge. The disadvantages of sponge zirconium are essentially the same as those of crystal-bar zirconium, and it is not generally as corrosion resistant. The advantage of sponge is its lower cost, approximately one-third that of crystal-bar zirconium.

ZIRCONIUM-TIN ALLOYS

Additions of 0.5 to 5 percent of tin to zirconium reduce the sensitivity of the corrosion resistance of zirconium to contaminants. Thus, a 5-percent-tin alloy can contain as much as 1500 ppm of nitrogen and be corrosion resistant in 600°F water. The addition of tin also increases the strength of zirconium at both room and elevated temperatures. Because of their higher strength at elevated temperatures, tin alloys require higher fabrication pres-

tures or temperatures than unalloyed zirconium. However, their ductility is good and does not limit hot fabricability. Five percent of tin decreases the thermal conductivity of zirconium by 50 percent.

ZIRCONIUM ALLOYS CONTAINING IRON, NICKEL, AND CHROMIUM

Evidence is accumulating which suggests that iron, nickel, and chromium have a beneficial effect on the corrosion resistance of zirconium in hot water and steam. Thus, of a number of alloys tested at MIT in 900°F, 1500 lb/sq in. steam, the most corrosion resistant contained 0.86 percent nickel and 0.4 percent iron. It is believed, however, that much smaller amounts of these materials have a pronounced effect. For example, MIT found 160 ppm of iron in a corrosion-resistant sample of crystal bar, and only 35-65 ppm in samples that were not corrosion resistant. No other significant differences of composition were found. In a number of arc-melted samples of sponge zirconium-2.5% tin alloys, WAPD found that the only samples which did not fail in 100 days at 650°F contained more chromium than the others.

These data, although not conclusive, do suggest strongly that small additions of iron, nickel, and chromium will have a beneficial effect on the corrosion resistance of zirconium alloys in water and steam. Therefore, the alloy selected contains 1.4-1.6 percent tin, 0.10-0.15 percent iron, 0.08-0.12 percent chromium, and 0.04-0.06 percent nickel, with a sponge zirconium base.

The MIT experience with higher nickel and iron alloys suggests the possibility of obtaining adequate corrosion resistance at higher temperatures than are now being considered, 600°F.

HIGH-TEMPERATURE ALLOYS

The high-temperature strength of pure zirconium is low, and work has been in progress to improve it. It has been found that additions of tin, molybdenum, niobium, titanium, and aluminum increase the high-temperature, short-time strength of zirconium to that of stainless steels. The same advantages in creep strength are not obtained, however, because the softening temperature of zirconium is low. The creep strength of the alloys which have been produced so far appears to be only about one-fifth that of stainless steel at a temperature of 930°F. However, further improvement is likely as this work progresses.

ABUNDANCE AND AVAILABILITY

Zirconium minerals are widespread over the earth. The principal zirconium minerals are zircon (ZrSiO_4), zircite (ZrO_2), and baddeleyite (ZrO_2). Commercial sources at the present time are the United States (Florida and North Carolina), Brazil, Ceylon, India, and Australia. The ore reserves of the United States are estimated to contain about $2\frac{1}{2}$ million tons of zirconium. All ores of zirconium contain hafnium, generally in amounts of from $\frac{1}{2}$ to 3 weight-percent, but sometimes as high as 20 weight-percent.

The rate of production of zirconium has increased greatly during the past few years, and at the same time, the quality of the material has improved markedly. These changes have been brought about by the great interest of the AEC in zirconium.

Essentially all the sponge zirconium has been produced by the Bureau of Mines at Albany, Oregon. A recent development, however, is the proposed construction and operation of a plant by the Carborundum Metals Company, Inc., to produce 150,000 lb/yr of sponge.

EXTRACTION AND PURIFICATION

Since hafnium is chemically very similar to zirconium, it is not removed by normal processing operations. Owing to the high thermal-neutron cross section of hafnium, it is necessary to use special processing techniques for hafnium removal if the zirconium is to be used in a thermal reactor. The processing operations are:

(1) Zirconium cyanonitride is produced by reacting a mixture of carbon and zircon ore (ZrSiO_4) in single-electrode, d-c arc furnaces. Large, square, graphite electrodes are used, which have a central hole through which air is introduced into the melt. Production is batch type. After reaction, each batch is allowed to cool, and the cyanonitride mass is removed and crushed.

(2) The cyanonitride is chlorinated in a reaction vessel about 5 ft in diameter and 20 ft long. The cyanonitride is fed in the top while chlorine is introduced at the bottom. The chlorination is exothermic, and a water spray maintains the steel-shell temperature at 1470°F.

(3) Hafnium is removed.

(4) In the past, zirconium chloride was purified by distillation and reduced by magnesium in separate retorts. This method is being replaced by the combination P-R (purification-reduction) process, in which both processes are carried on in the same retort.

In the P-R process, a long retort is used. The magnesium is loaded into the bottom of the pot, and the zirconium tetrachloride into a pan near the top. The retort is then heated, volatilizing the chloride which reacts with molten magnesium in the lower portion of the furnace to produce zirconium.

The mass of zirconium sponge contains magnesium chloride and residual magnesium, most of which is removed by heating in a vacuum chamber to 1690°F. The zirconium is then graded and crushed.

There are several grades of zirconium sponge. "A" sponge is a dense mass formed as a ring around the retort. It is quite pure and can be arc melted quite readily. "B" sponge is also dense and forms on the bottom of the retort. It is the first material formed and is least pure. It too can be arc melted readily. "C" sponge is the last material formed and is a spongy mass. It is quite pure but entraps a considerable amount of magnesium chloride causing it to spatter considerably in arc melting. Occasionally, there is no sharp demarcation between the various grades of sponge. This material is classed as "F" sponge.

The zirconium sponge produced in this final step can be used as melting stock, or it can be refined to increase the purity. A few years ago the sponge zirconium produced was considerably less pure than it is today, and the corrosion resistance of the material after melting was unsatisfactory. Currently, however, a purer sponge zirconium is being produced, and the material has greatly improved corrosion resistance in hot water.

(5) Sponge zirconium can be refined using the de Boer iodide process. In this operation, the major contaminants removed are nonmetallic materials, such as oxide and nitride, and magnesium which is normally present in fairly large amounts in sponge. The crystal-bar zirconium which is produced is softer and more ductile than the sponge and, in general, possesses better corrosion resistance.

The production units in which the iodide-refining process is carried on are metal cylinders 1 to 2 ft in diameter and 4 ft or more long.

The sponge is loaded into the reactor chamber between a molybdenum screen and the wall of the unit. Iodine is introduced into the evacuated (pressure of 0.01 to 0.1 micron) chamber, and a surrounding heating bath is brought to 570°F. After the reaction starts,

this bath serves to remove heat. The iodine reacts with the sponge to form ZrI_4 , which first vaporizes and then dissociates on a zirconium wire heated electrically to about 2190°F. The liberated iodine is free to recombine with the sponge and continue the process.

Crystal-bar zirconium is corrosion tested for two weeks in 650°F water. If at the end of this time, there are no traces of white corrosion product, the material is classed as Grade I.

The compositions of typical lots of currently produced sponge and crystal-bar zirconium are shown in Table 1.24.1.

Table 1.24.1—Typical Analyses of Currently-produced
Crystal-bar and Sponge Zirconium

Element	Amount detected, ppm	
	Westinghouse crystal bar	Bureau of Mines sponge
Al	40	30
B	None	< 0.2
C	20	95
Ca	< 50	Not reported
Cd	None	< 21
Co	None	< 2
Cr	30	15
Cu	< 5	30
Fe	200	650
Hf	85	85
Mg	< 10	100
Mn	< 10	20
Mo	< 10	Not reported
N ₂	10	40
Ni	40	< 2
O ₂	100–200	600–1000
Pb	< 10	70
Si	20	20
Sn	< 10	Not reported
Tl	10	< 50
V	None	< 10

The differences in properties between crystal-bar and sponge zirconium can be explained almost entirely in terms of the differences in their oxygen and nitrogen contents. This amount of oxygen is sufficient to cause a significant increase in hardness and strength of zirconium at room temperature and to raise the temperature of transformation from the alpha to the beta phase. The difference in nitrogen content decreases the corrosion resistance of sponge zirconium in hot water.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants and the effects of temperature on some of these constants are given in Table 1.24.2 and Figs. 1.24.1 to 1.24.3.

Table 1.24.2 — Physical and Chemical Constants of Zirconium

Thermal-neutron-absorption cross section, barns/atom	0.18 ± 0.02
Density,* gm/cm ³	
Alpha, room temperature	6.50
Alpha, 863°C (estimated)	6.36
Beta, above 863°C	6.40
Melting point, °C	1845 ± 25
Heat of fusion, kcal/mole	5.5
Heat of vaporization, kcal/mole	125
Specific heat,† cal/(mole)(°C)	
Room temperature	6.32
127°C	6.74
427°C	7.43
727°C	7.86
862°C(α)	8.03
862°C(β)	7.27
1127°C	7.27
Enthalpy (H _T - H _{25°C}), cal/mole	
127°C	665
427°C	2800
727°C	5095
862°C(α)	6170
862°C(β)	7090
1127°C	9015
Entropy (S _T - S _{25°C}), cal/(mole)(°C)	
127°C	1.91
427°C	5.88
727°C	8.60
862°C(α)	9.61
862°C(β)	10.42
1127°C	11.64
Electrical resistivity, μohm-cm	‡
Coefficient of linear thermal expansion (25°C), per °C	
c - axis	6.15 × 10 ⁻⁶
a - axis	5.69 × 10 ⁻⁶
For temperatures from 0° to 600°C, the linear thermal expansion coefficients are:	
c axis: $2.418 \times 10^{-6} + 0.01249 \times 10^{-6} T$	
a axis: $5.357 \times 10^{-6} + 0.00109 \times 10^{-6} T$	
where T is in °K. These values were determined for a 2.4 wt-percent hafnium alloy, but probably differ little from those for hafnium-free zirconium	
For worked and alpha-annealed material	
Thickness	6.7 to 10.1 × 10 ⁻⁶
Transverse	4.8 to 6.3 × 10 ⁻⁶
Longitudinal	4.6 to 5.9 × 10 ⁻⁶
Thermal conductivity,‡,¶ watts/(cm)(°C)	
The formula below is a useful approximation for engineering purposes of the correlation between thermal and electrical conductivities:	
$K = 0.0308 (\sigma - 0.00327) T + 0.0381$	
where:	
K = thermal conductivity, watts/(cm)(°C)	
σ = electrical conductivity, (μ ohm-cm) ⁻¹	
T = temperature, °K	

Table 1.24.2 — (Continued)

Crystal structure and allotropic

The alpha-to-beta transformation temperature is $863^{\circ} \pm 3^{\circ}\text{C}$

Alpha-zirconium has a hexagonal close-packed lattice with $a_0 = 3.2321 \text{ \AA}$ and $c_0 = 5.1474 \text{ \AA}$

Beta zirconium, which is stable to the melting point, has a body-centered cubic lattice with $a_0 = 3.16 \text{ \AA}$ at 867°C

* $\text{Gm/cm}^3 \times 62.43 = \text{lb/cu ft}$

† $\text{Cal}/(\text{mole})(^{\circ}\text{C}) \times 1 = \text{Btu}/(\text{lb-mole})(^{\circ}\text{F})$

‡See Fig. 1.24.1 for the electrical resistivity of zirconium; see Fig. 1.24.2 for the electrical resistivity of some zirconium alloys

§ $\text{Watts}/(\text{cm})(^{\circ}\text{C}) \times 0.239 = \text{cal}/(\text{sec})(\text{cm})(^{\circ}\text{C})$

$\text{Cal}/(\text{sec})(\text{cm})(^{\circ}\text{C}) \times (2.419 \times 10^2) = \text{Btu}/(\text{hr})(\text{ft})(^{\circ}\text{F})$

¶See Fig. 1.24.3 for the thermal conductivity of zirconium and some of its alloys

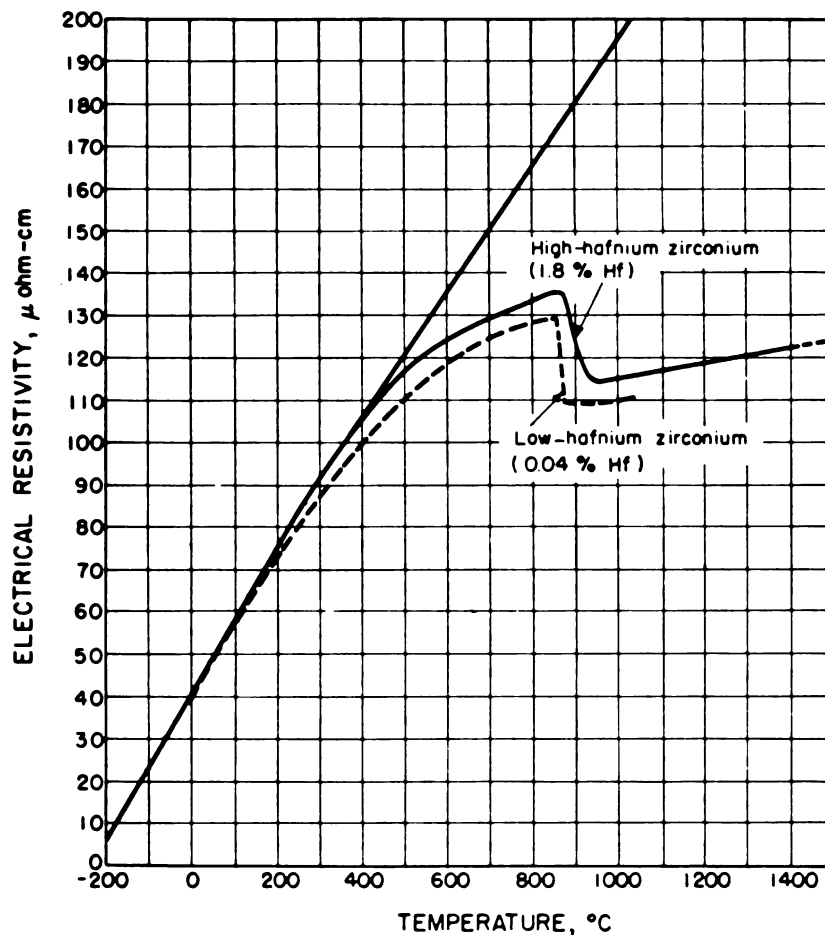


Fig. 1.24.1—The Electrical Resistivity of Zirconium as a Function of Temperatures. Reprinted from L. A. Cook, et al, Preliminary Report on the Electrical Resistivity of Zirconium, WAPD-25, Dec. 20, 1950.

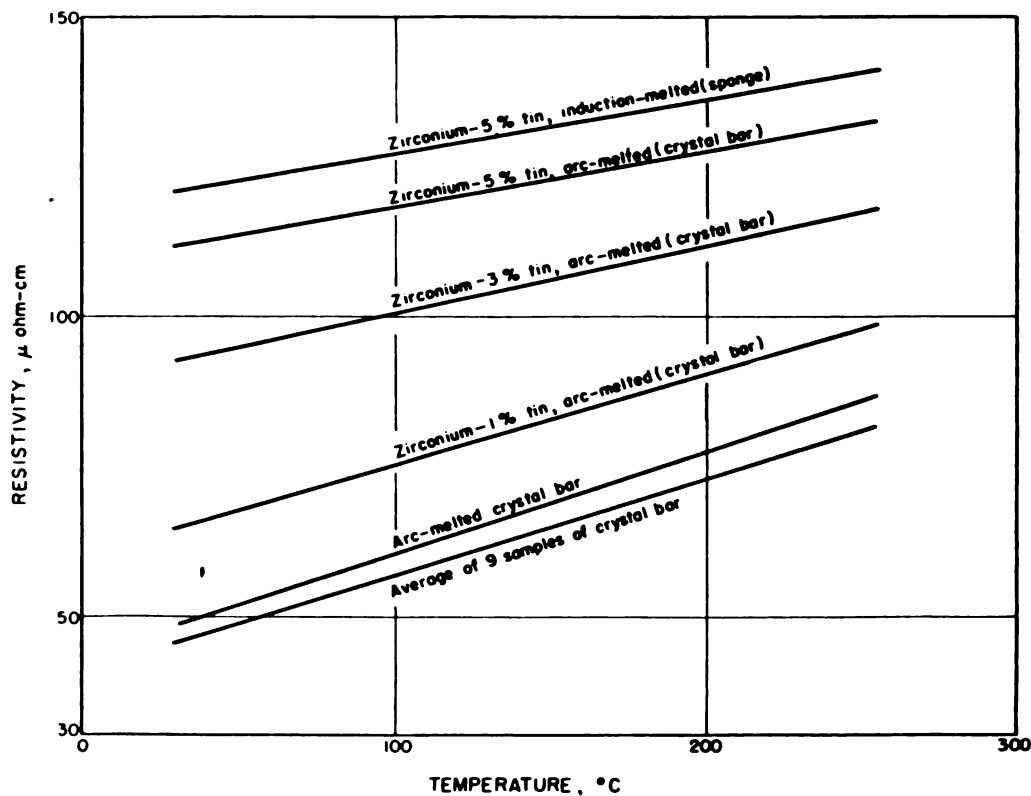


Fig. 1.24.2 — The Electrical Resistivity of Some Zirconium Alloys as a Function of Temperature. Prepared from data of George Bing, *The Thermal and Electrical Conductivity of Zirconium and Its Alloys*, BMI-65, April 16, 1951.

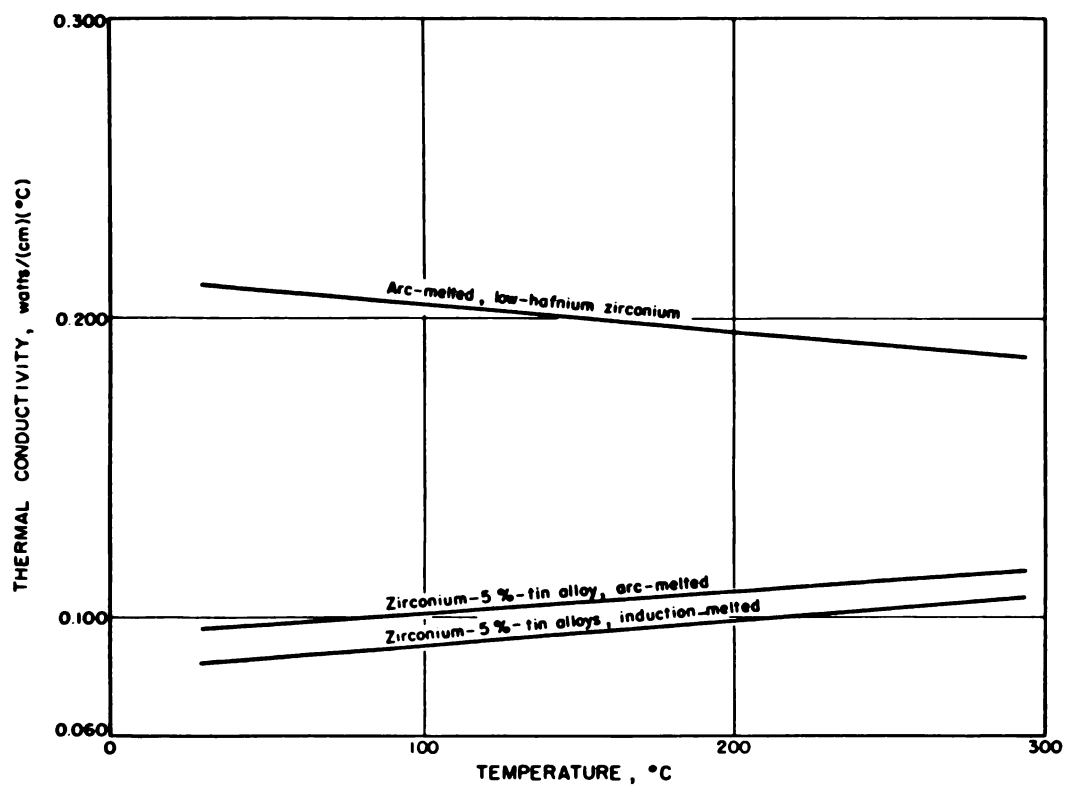


Fig. 1.24.3 — The Thermal Conductivity of Zirconium and Some Zirconium Alloys as a Function of Temperature. Prepared from data of George Bing, The Thermal and Electrical Conductivity of Zirconium and Its Alloys, BMI-65, April 16, 1951.

MECHANICAL PROPERTIES

TENSILE STRENGTH

Very pure zirconium is soft, ductile, and weak. Furthermore, its strength is decreased markedly by heating to moderate temperatures. As with all very pure materials, tiny amounts of impurities have a large effect on strength. This fact is indicated in Fig. 1.24.4. The data given in this figure show that by using the best current crystal-bar zirconium and by processing it by painstaking methods to avoid contamination, the strength can vary in the ratio of 2:3. The data in this figure also show how sensitive zirconium is to small additions of oxygen. One tenth percent of oxygen increases room-temperature strength by approximately 50 percent. It is also interesting to note that crystal-bar zirconium with 0.1 percent oxygen added has essentially the same strength as recent Bureau-of-Mines sponge zirconium which has been arc melted.

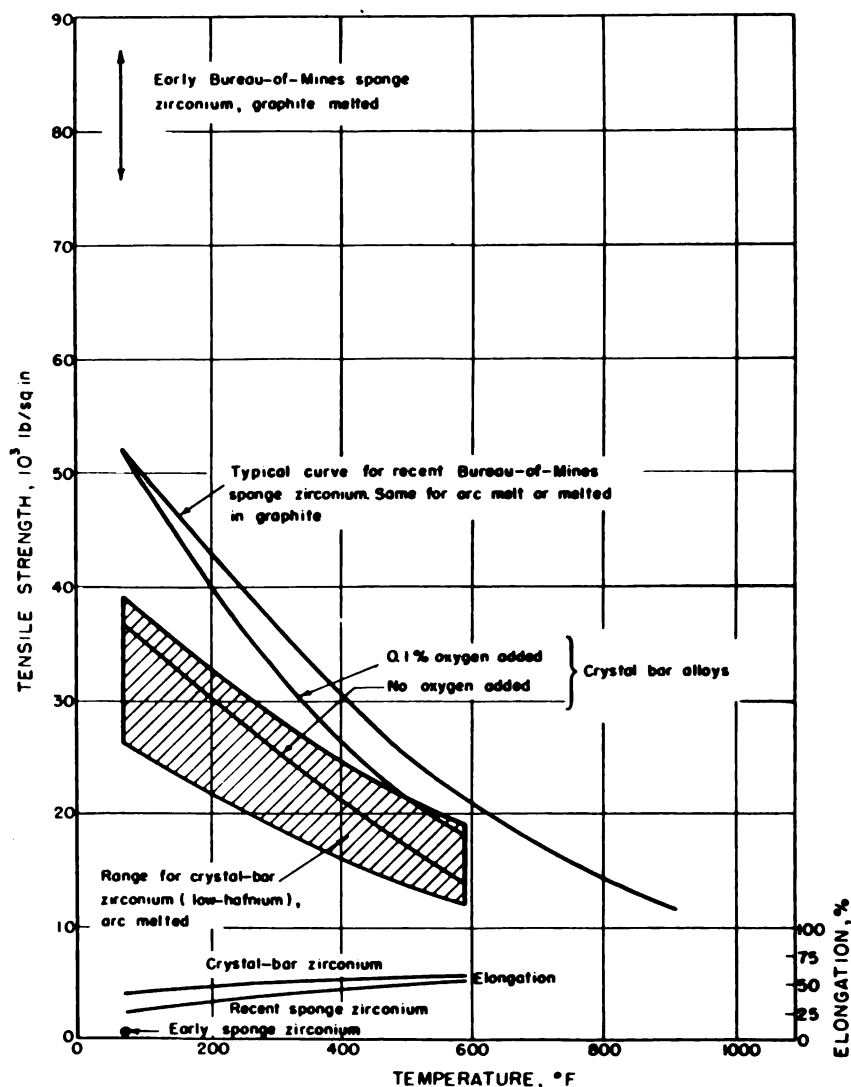


Fig. 1.24.4 — The Tensile Properties of Zirconium. Prepared from scattered data in reports of BMI, Bureau of Mines, MIT and WAPD, Aug. 15, 1952.

It is apparent from these data that current Bureau-of-Mines sponge zirconium has very different characteristics from material which was produced a few years ago. This early material had nearly twice the room-temperature tensile strength of sponge zirconium and nearly three times the strength of arc-melted crystal-bar zirconium. The ductility of this early sponge material was correspondingly much lower than either that of current sponge or crystal-bar production.

Because the strength of zirconium is initially low and becomes still lower at reactor temperatures, attempts have been made to improve the strength of zirconium by alloying. In much of this work, additions were desired which would not harm the corrosion resistance of zirconium in hot water. One such addition which has been tried is oxygen. However, as can be seen in Fig. 1.24.4, the hardening effect of oxygen was largely lost at only moderately elevated temperatures. Another addition, tin, has a hardening effect which is retained at elevated temperatures; this can be seen from the data given in Fig. 1.24.5.

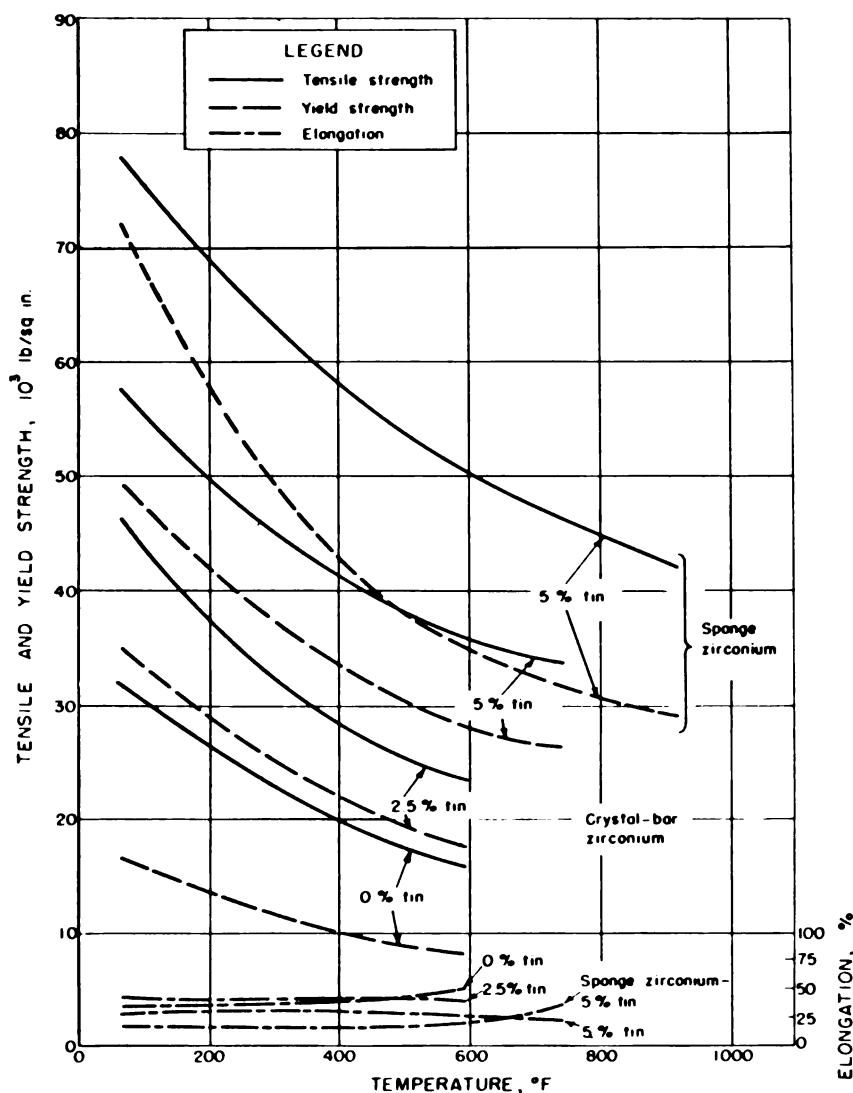


Fig. 1.24.5 — The Tensile Properties of Zirconium-Tin Alloys. Prepared from scattered data in BMI and WAPD reports, Aug. 15, 1952.

Other work has been in progress to greatly increase the high-temperature strength of zirconium alloys without regard to corrosion resistance in hot water. Some of the stronger alloys thereby produced have the tensile properties shown in Fig. 1.24.6. The data in Fig. 1.24.6 show that the short-time tensile properties of the zirconium alloys approach those of stainless steels. Their creep properties, however, are inferior. (See also subsequent discussion of creep.)

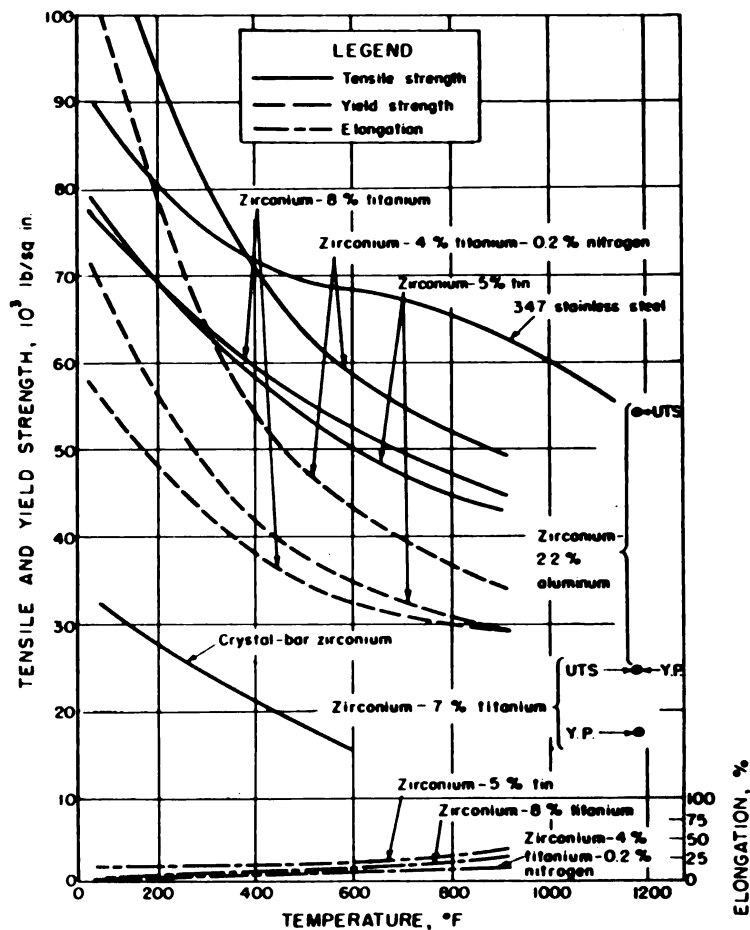


Fig. 1.24.6 — The Tensile Properties of Selected High-strength Bureau-of-Mines Sponge-zirconium Alloys. Prepared from scattered data in BMI and Bureau of Mines reports, Aug. 15, 1952.

It should be remembered that this alloying work is still in a rather early stage and that stronger alloys may be produced. The alloys which have been discussed are all solid-solution alloys, and it is expected that additions of other materials which form a fine precipitate will cause a further improvement in the properties.

EFFECT OF COLD WORK AND RECRYSTALLIZATION

Zirconium can be hardened greatly by cold work. Fifty percent cold work, for example, increases the tensile strength of a particular lot of zirconium from 50,000 lb/sq in. to

90,000 lb/sq in. Hard-drawn 0.017-in. wire may have a tensile strength of 123,000 lb/sq in. The ductility of such material is low, 2 percent.

This cold-working effect is annealed out at rather moderate temperatures, as can be seen in Fig. 1.24.7. Annealing at 930°F will greatly reduce strength and increase ductility.

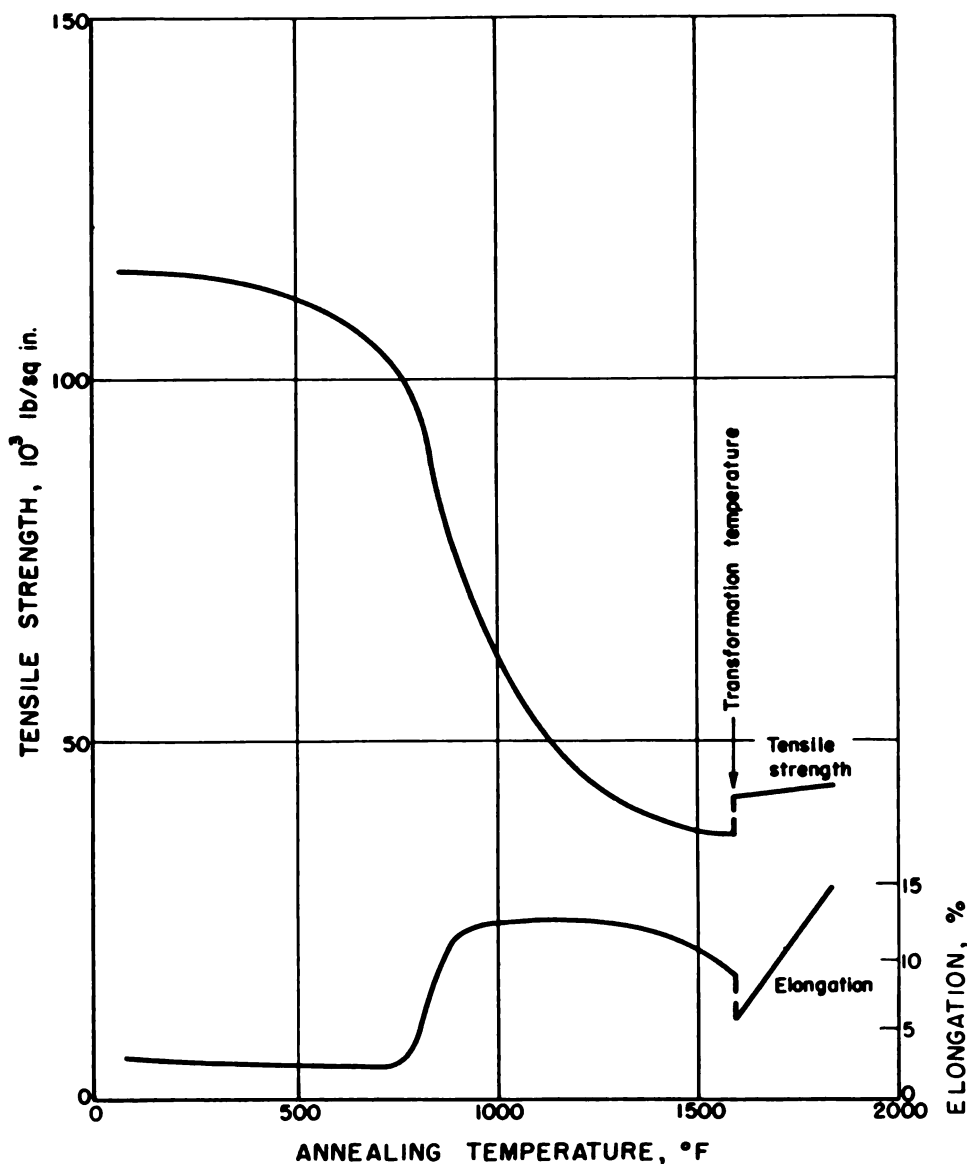


Fig. 1.24.7 — The Effect of Annealing Temperature on the Tensile Properties of Cold-swaged Zirconium. Data from J. D. Fast, *Metallwirtschaft*, Vol 17, 1938.

If annealing is done at temperatures slightly higher than the transformation temperature, some hardening occurs, as indicated in Fig. 1.24.7.

MODULUS OF ELASTICITY

The modulus of elasticity of pure zirconium decreases linearly from 13.8×10^6 lb/sq in. at room temperature to 10.5×10^6 lb/sq in. at 600°F.

HARDNESS

Hardness measurements made on pure zirconium and certain zirconium alloys over a wide temperature range are reported in Fig. 1.24.8. From this plot, it is apparent that there is a large, uniform decrease of hardness with increasing temperature nearly up to the transformation temperature (1585°F in the case of pure zirconium and a little higher for zirconium-tin alloys). The softening rate of zirconium and zirconium-tin alloys be-

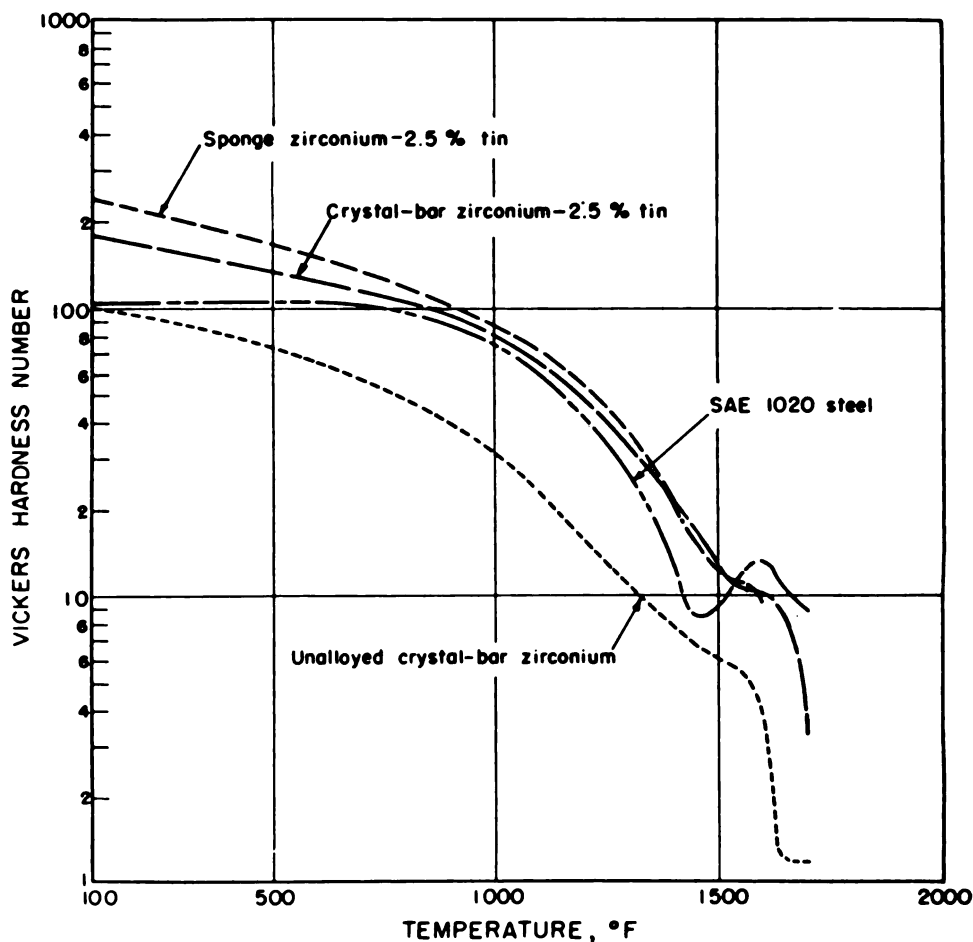


Fig. 1.24.8 — The Hot Hardness of Some Arc-melted Zirconium Alloys. Assembled from scattered data in BMI reports, Aug. 15, 1952.

comes low below the transformation temperature before dropping off rapidly at the transformation temperature. This produces the step seen in three of the curves in Fig. 1.24.8. The same increase in strength just below the transformation has been in hot tensile tests, and was attributed to precipitation of an unknown phase.

Oxygen also has a hardening effect, as seen by the higher hardness of the sponge alloy at room temperature. This hardening effect, however, is essentially all lost at 1000°F.

For comparison, results of hardness determinations are given for a sample of SAE-1020 steel. The important differences between its hardness-temperature curve and that

for zirconium alloys is the absence of softening at temperatures under 800°F and a more exaggerated variation in hardness around the transformation temperature. The hardness, however, is not greatly different from that of zirconium alloys.

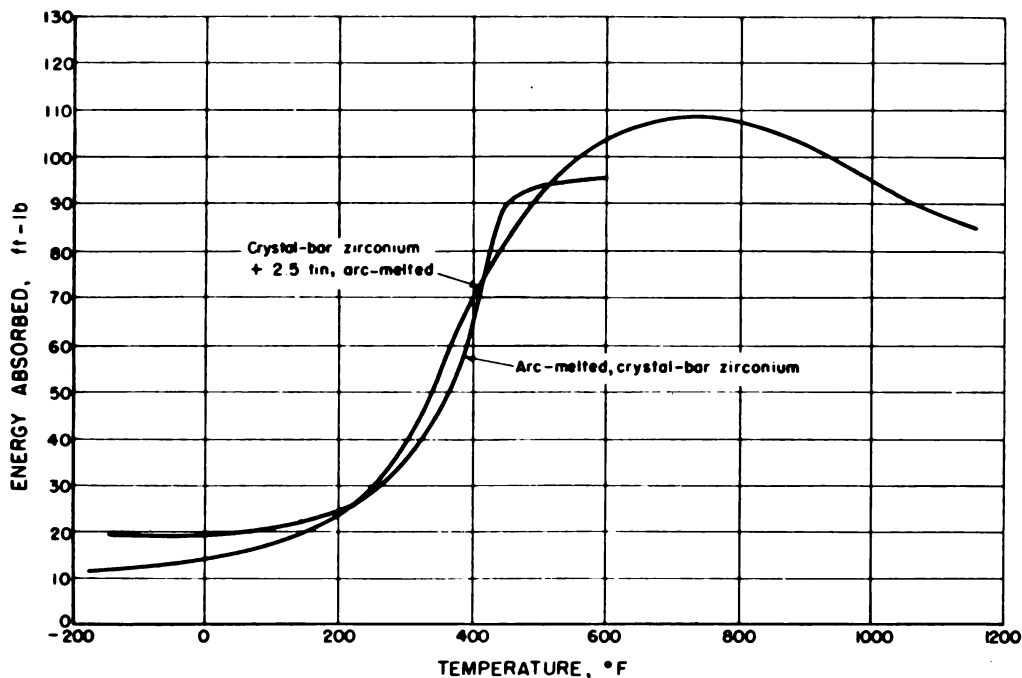


Fig. 1.24.9—V-Notch Charpy Impact Tests on Arc-melted Zirconium and Zirconium-2.5% Tin Alloy. Reprinted from R. W. Dayton, et al, Hydrogen Embrittlement of Zirconium, BMI-767, Aug. 22, 1952.

IMPACT AND AGING

Zirconium and its alloys generally have relatively low impact strength at room temperature. At about 400°F, however, there is a transition, and above this temperature, the impact strength is high. As the temperature is increased beyond 750°F, softening of the material lowers the impact strength. This behavior is illustrated in Fig. 1.24.9. Even at temperatures as low as minus 150°F, zirconium or zirconium-tin alloys are not excessively brittle. Although, in the notch-bar test, the impact strength at such low temperatures is only 10 to 20 ft-lb, there is appreciable plastic deformation before fracture.

The effect is not observed in tensile tests of unnotched bars, which show little change in ductility between room temperature and 600°F. Furthermore, tensile tests at room temperature made at a very high strain rate do not give significantly different results than are obtained in slow-speed testing.

Lustman and Mudge at WAPD found that the loss of impact strength at room temperature was a precipitation effect traceable to small amounts of hydrogen which are generally present in zirconium. It appears that at moderate temperatures, of the order of 500° to 700°F, the small amounts of hydrogen contained in normal zirconium are held in solution. When cooled below this range, the decrease in solubility appears to be sufficient to cause precipitation of the hydride phase. This precipitation occurs below 500°F, possibly at

temperatures as low as 300°F. If the rate of cooling is relatively slow, that is, air cooling in sections of moderate size, the hydride phase precipitates as plates along crystallographic planes.

The impact strength of specimens cooled relatively slowly in the temperature range below 600°F is low, 10 to 20 ft-lb. If quenched from 600°F, the impact strength at room temperature is as high as is observed in normal zirconium at 600° to 700°F, 40 to 70 ft-lb. Since hydride platelets cannot be seen in quenched samples and can be seen frequently in slowly cooled samples, it is believed that the hydride platelets are the cause of the brittleness.

Additional information which supports this hypothesis is that when hydrogen is removed from zirconium by annealing in a very good vacuum at a very high temperature, material which otherwise could be embrittled was ductile, regardless of heat treatment. Furthermore, when 500 ppm of hydrogen was added to zirconium which could not be made brittle by heat treatment alone, the material was brittle.

It appears that zirconium is as sensitive to the effect of small amounts of hydrogen as it is to so many other things. Hydrogen assays on zirconium which can be embrittled show that only 30 to 70 ppm of hydrogen are present. A sample of material which could not be made brittle by heat treatment alone contained 12 ppm of hydrogen.

In order to remove hydrogen from zirconium, it appears necessary to extract the hydrogen in a good vacuum at a high temperature. The high temperature is not required to speed up the diffusion of hydrogen within the zirconium, because diffusion is rapid even at 600°F. The high temperature is necessary to increase the pressure of hydrogen in equilibrium with the small concentration in normal samples to the point where vacuum equipment is adequate.

CREEP STRENGTH

Only scattered data are available on the creep strength of zirconium and its alloys.

Alloys of zirconium naturally have considerably higher creep strength at 500°F than unalloyed zirconium. At this temperature, crystal-bar zirconium creeps at a rate of 10^{-4} percent/hr at a stress of 14,000 lb/sq in. Zirconium:2.5% tin alloy has a secondary creep rate of 10^{-5} percent/hr at a stress of 20,000 lb/sq in.

The creep strengths of a few other alloys at 930°F are given in Fig. 1.24.10, where they are compared with stainless steel at the same temperature and with crystal-bar zirconium at 500°F.

Time-to-rupture data on crystal-bar zirconium at a temperature of 500°F are given in Table 1.24.3.

POISSON'S RATIO

Poisson's ratio for pure zirconium at room temperature is 0.32 to 0.35.

FATIGUE STRENGTH

Few fatigue studies have been made on zirconium and its alloys. At a temperature of 500°F, the following flexural fatigue data have been obtained.

Stress, lb/sq in.	Life, cycles
8500	5.2×10^6
8500	8.6×10^6
8250	3.8×10^7 *
8000	9.7×10^7 *

*Did not fail

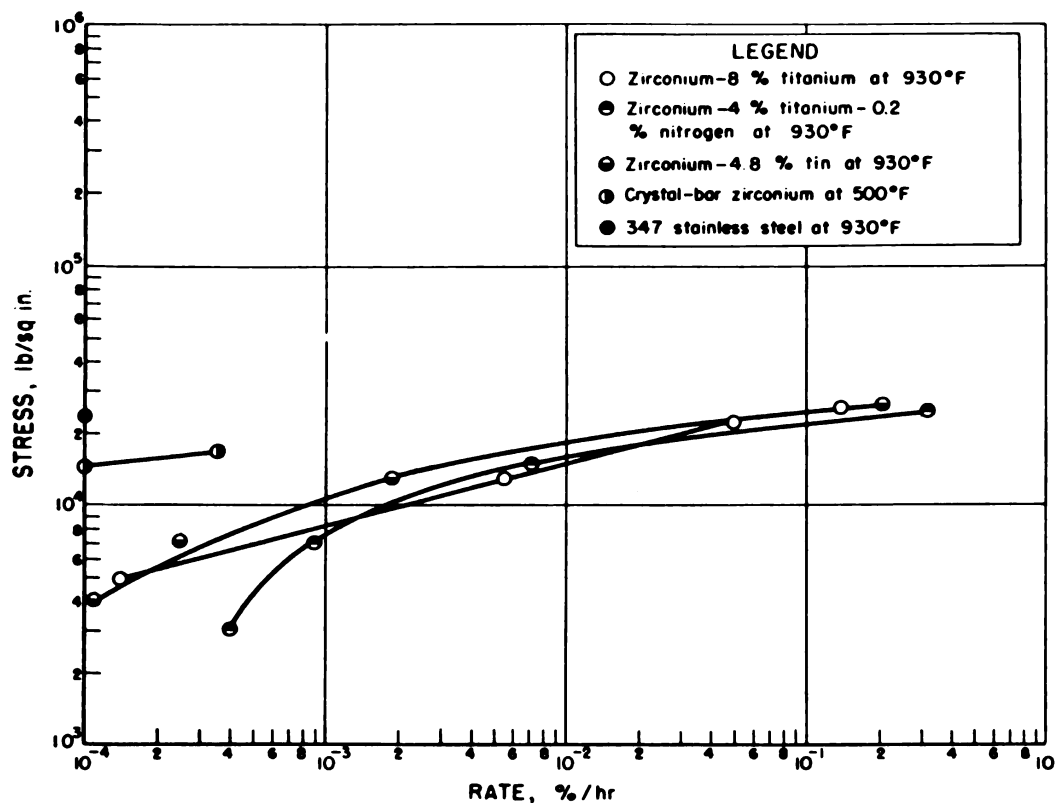


Fig. 1.24.10—The Creep Properties of Zirconium and Some Zirconium Alloys Compared With Type-347 Stainless Steel. Prepared from data of BMI Progress Reports for months of October 1951 and August 1952, BMI-710 and BMI-769, November 1, 1951 and September 1, 1952.

Table 1.24.3 — Creep-rupture Data on Arc-melted Crystal-bar Zirconium at 500°F

(Creep-rupture Tests of WAPD Grade I Iodide Crystal-bar Arc-melted Zirconium at 260°C, WAPD-39, November 24, 1951)

Time to rupture, hr	Stress, lb/sq in.	
	Longitudinal direction	Transverse direction
10	18,000	14,000
100	17,000	14,000
1000	16,000	13,000

Some data are available on a 2.5-percent-tin alloy at a temperature of 500°F. These tests were made in an axial-load fatigue machine in which the stress was always tensile and in which the minimum tensile stress was $\frac{1}{10}$ of the maximum. On unnotched specimens at a stress of 23,000 lb/sq in., failure occurs in from 700,000 to 950,000 cycles. On notched fatigue specimens in which the notch causes a theoretical stress concentration factor of 2.8, failure occurs in 10^7 cycles at a stress of 19,000 lb/sq in.

FRICTIONAL PROPERTIES

Zirconium and its alloys gall with the greatest ease when rubbed against themselves or against materials with which they are commonly used, such as stainless steel. For that reason, it sometimes is necessary to attach a wearing surface to a zirconium part, using a material which is better able than zirconium to resist galling and scoring. In some applications, as in wire drawing, it is possible to obtain satisfactory frictional behavior by the use of a compounded lubricant or by a coating. In general, however, such a solution is not usable.

MELTING AND CASTING

In most respects, zirconium can be fabricated readily; however, this generality decidedly does not apply in the case of melting. Few materials are as difficult to melt satisfactorily as zirconium and its alloys because zirconium is an extremely reactive material, has a high melting point, and is extremely sensitive to small amounts of contaminants. Every known crucible material has been attacked to some degree by molten zirconium, and crucible melting, which otherwise would be ideal for the preparation of zirconium and zirconium-alloy ingots, can thus be used only when the contamination that is introduced can be tolerated.

Accordingly, most of the zirconium has been arc melted. This operation, however, is far from any conventional arc-melting method. Since satisfactory crucibles for the material are not known, it is necessary to melt the material in a watercooled copper crucible so that the crucible material is never in contact with molten zirconium. Instead, a layer of frozen zirconium is really the crucible for the molten material. Because of rapid heat loss by conduction from the molten zirconium to the solid zirconium and the crucible walls, the arc power required for melting is high, and even so, the molten pool is rather small. This gives rise to a serious homogeneity problem when alloys are being produced.

For melting zirconium the chopped feed stock is fed into the melt slowly. At one time, the feeding was almost continuous. However, the solid feed material often drops to the bottom of the molten pool without melting and entraps argon from the atmosphere under which melting is done producing voids. This difficulty has been avoided by the so-called "long-arc" technique. In this technique, no charging is done when the arc power is at a maximum and the arc length is short. Periodically, the arc is lengthened and its power reduced correspondingly. This permits the molten charge to solidify partially so that its top surface becomes mushy. A new charge is then added and the arc length again decreased. The new charge, as well as the original surface of the ingot, then melts and forms a bath free of voids.

The same technique has been used for melting zirconium-tin alloys. In this case, each small charge added has the proper average composition desired in the finished ingot. Owing to the deficiencies of the arc-melting process, thorough mixing does not occur, and the once-melted ingots are not homogeneous. However, by forging and rolling the ingots to sheets, cleaning and chopping the sheets into small pieces, and remelting, it is possible to produce zirconium alloys of excellent homogeneity.

One consistently troublesome problem has been that of tungsten inclusions in the melted ingots. When the feed stock is a type which melts quietly, little difficulty is experienced. However, occasionally, molten zirconium will splash onto the tungsten electrode with the result that a piece of the electrode loosens and drops into the melt. The tungsten does not always dissolve and gives trouble in subsequent fabrication.

When crystal-bar feed stock is used, excessive difficulty with tungsten inclusions does not result. Sponge zirconium, however, as produced by the Kroll process contains magnesium chloride which is hygroscopic and absorbs water on exposure to the atmosphere. On melting this material, violent spattering occurs causing severe erosion of tungsten electrodes. This led the Bureau of Mines to develop a consumable electrode arc-melting process. The zirconium sponge to be melted is cold pressed into two-inch-square electrodes. These are fastened together and used as the electrode in the arc-melting process. The electrode is both the source of heat and of all the zirconium in the ingot. Spattering is not a problem in this process, because its only adverse effect is a poor ingot surface in the first melting operation, and this can be removed by either machining or remelting.

The only other arc-melting electrode material which has received much consideration is graphite. The difficulty with graphite is that some carbon is picked up by the melt, and this carbon affects the corrosion resistance of the material adversely. However, tin could be used to improve corrosion resistance. Other electrode materials have been tried, but none tested so far have offered significant advantages.

It has been mentioned that molten zirconium attacks all crucibles with which it is in contact. A considerable amount of study has been devoted to the problem of satisfactory crucibles for zirconium and titanium. Experience has shown that all oxides tested have been attacked, giving up sufficient oxygen to the zirconium so that serious embrittlement occurred. Work on this subject is continuing; thoria, cerium sulfide, and stabilized zirconia offer some promise, although the reports on the use of cerium sulfide are conflicting.

Of all crucible materials tested, graphite appears to offer the most promise. Although 0.3-0.4 percent of carbon is dissolved under adverse conditions, carbon-pickup can be reduced below 0.1 percent by using good control and large-scale melting equipment. The major effect of the carbon is to reduce corrosion resistance, but this effect can be balanced by alloying the zirconium with tin. Zirconium carbide also has an adverse effect on the ductility of the ingot. However, by gentle handling of the ingot during its initial forging, the carbide network is broken up, and the material can then be processed normally.

In the work which has been done so far with graphite crucibles, both induction and resistance heating of the graphite crucible have been used. Either type of crucible-melting offers the advantage that melting can be carried out in a vacuum to remove volatile impurities and avoid entrapped gas which may form voids. Furthermore, by melting all of the charge at the same time, homogeneity can be attained. In this respect, such melting methods possess a considerable advantage over arc melting.

Some attention has also been given to more novel methods of melting. One, an arc-melting method call "skull" melting, appears worthy of more consideration for the production of zirconium alloys. In this method, a molten pool is formed by an arc on the top surface of a large piece of zirconium. The central part of the zirconium is melted and then poured into a mold. In this way, a greater degree of homogeneity can be achieved than in conventional arc melting.

A method related to skull melting consists of melting a part of the top surface of a large block of zirconium by using a flat, spirally wound induction coil. The molten material produced in this method can be poured, or new feed stock can be added through the center of the induction coil to build up the top surface and produce a billet.

Another melting method, which appears to be useful only for small-scale melting, is "drip" melting. In this method, a bar of zirconium is fed slowly through an induction coil. The material melts and drips off the bottom of the bar into an ingot. This does not appear

to be an especially attractive method for preparing alloys and suffers from the disadvantage that cold shuts are apt to be present.

FORMING AND FABRICATION

Because of their ductility, zirconium and its alloys can be fabricated readily. All conventional fabrication methods can be used with these materials. However, certain precautions must be observed.

At elevated temperatures, zirconium oxidizes moderately rapidly. At a good hot-fabricating temperature, 1450°F, the rate of oxidation is from 0.5 to 1 mil in one-half hour in air. This rate is not excessive for rough-finishing operations. However, for parts for which this amount of oxidation cannot be tolerated, protection either by an atmosphere or by jacketing is essential. Heating in a salt bath or a lead bath also is a possibility, though little work on such methods has been done. Protection by an atmosphere is generally incomplete in normal practice, with the result that considerable oxidation still occurs. An inert gas atmosphere such as argon or helium should be used. Atmospheres containing hydrogen are unsatisfactory.

Because of the low rate of diffusion of oxygen and nitrogen in the alpha-phase region, contamination is essentially confined to the surface film. This is not true when working at temperatures above the transformation (above 1585°F), and such temperatures should be avoided except in operations, such as forging, where the contaminated skin can be removed. It is possible also to provide protection for fabrication operations at these temperatures by cladding. However, in this case, strict temperature limits must be observed. Zirconium forms eutectics with the normal jacketing materials, and working should proceed below the eutectic temperature. The eutectic temperatures are approximately 1600°F for copper, 1700°F for iron, and 1750°F for nickel. Some use has been made of copper jackets for extrusion above the eutectic temperature, but it is presumed that the zirconium and copper surfaces were not sufficiently clean to permit alloying in this one-pass operation.

FORGING

To prevent contamination and loss of material, ingots should be forged at as low a temperature as the forging equipment will allow. Generally, forging of pure zirconium and zirconium alloys is possible at temperatures of 1550°F. Because of the strengthening effect of tin and other materials, higher temperatures are necessary for alloys. Forging temperatures as high as 1800°F for 4- to 5-percent-tin alloys have been used. Cracking of ingots is not a problem, generally, unless the material has been melted in graphite. In this case, gentle forging is necessary until the carbide network has been broken up.

HOT ROLLING

Zirconium and its alloys can be hot rolled readily at a temperature of 1450°F. If the rate of oxidation is a problem at this temperature and heavy rolling-mill equipment is available, even lower temperatures can be used without danger of cracking. Temperatures as low as 1100° to 1200°F have been used satisfactorily. If the hardness of the zirconium alloy being rolled is excessive at 1450°F, higher temperatures can be used. Temperatures of 1600° to 1700°F have been used on tin alloys. Such practice is not to be recommended in general, however, because of the rapidity of oxidation at these temperatures. Some evidence exists showing that scaling is more rapid for tin alloys.

COLD ROLLING

The cold ductility of zirconium and most of its alloys is adequate at room temperature to permit ample cold rolling for any practical purpose. Reductions of 70 to 80 percent are feasible with pure zirconium and of 40 to 50 percent with Zr : 2.5% Sn alloys.

DRAWING

The ductility of zirconium is sufficient to permit fairly large reductions in cold drawing; however, difficulties are experienced with galling of the material against the die. Phosphate coatings or copper coatings are useful to prevent galling. The phosphate coating is applied by degreasing, pickling in an aqueous solution of 10 percent HNO_3 and 5 percent HF by volume, and then immersing in an aqueous solution of 1 percent H_3PO_4 and $\frac{1}{2}$ percent HF at room temperature until the metal surface is converted to an insoluble coating. The pickling solution removes the coating. Chlorinated oils have been used as lubricants, but a suspension of molybdenum disulfide, fumed lead oxide, and fumed zinc oxide in thinned lacquer has been more effective. Soap and wax have been useful lubricants for deep-drawing operations.

The deep-drawing characteristics of zirconium are satisfactory.

EXTRUSION

Zirconium has been extruded at temperatures from 750° to 2000°F. Both plates and tubing have been extruded. The feed stock has been ingots as well as sponge contained in copper jackets. In general, it is desirable to work at temperatures over 1300°F to avoid excessive extrusion pressures. As in wire drawing, galling of the zirconium and the die is a problem. Copper and steel jackets have been used to prevent difficulties of this sort.

Bundles of crystal bar as well as sponge have been loaded into cans and compacted and extruded simultaneously. After such a process, it is necessary to homogenize the material at a high temperature for a considerable time. Temperatures of 2000°F for a period of 12 hr have been used.

POWDER METALLURGY

Powder metallurgy compacts have been made from pure zirconium and zirconium-tin alloys. Because zirconium is an extremely ductile material, it is necessary to modify it in such a way that it can be crushed to a powder. This has been done by heating zirconium at 1470°F in purified hydrogen. Under these conditions, zirconium dihydride is produced which is extremely friable. If alloys are being produced, the zirconium powder is mixed with the alloying material, pressed at 20 to 60 tons/sq in. and sintered in vacuum at 2200° to 2370°F. In this way, it is possible to make powder-metallurgy products which have theoretical densities.

The greatest shortcoming of the powder-metallurgy process as applied to zirconium alloys is contamination by oxygen and nitrogen. These impurities are picked up from the hydrogen used, which must be specially purified to remove them as completely as possible. The oxygen hardens the material, and the nitrogen reduces its corrosion resistance. No materials have been made by the powder-metallurgy process which have as good corrosion resistance as well-made arc-melted and rolled products using the same alloying materials.

JOINING

BRAZING

It does not appear possible to make thoroughly satisfactory brazed joints on zirconium. A sound joint can be made using various commercial silver solders, but such joints develop layers of brittle intermetallic compounds, and the joints are not corrosion resistant in 600°F water. It does not appear likely that any corrosion-resistant brazed joint can be developed which is strong and tough, since all materials which might be usable appear to have been tested with negative results.

WELDING

In most respects, zirconium is an excellent material for welding. Because of its high affinity for most gases, welds made in zirconium are almost invariably sound. Because of its ductility, cracking of the welds does not occur, and the weld and the heat-affected metal are ductile. This is not true for Bureau-of-Mines sponge zirconium which has been melted in graphite. Welds of this material made with filler rod of the same material are brittle and tend to crack. This difficulty can be eliminated if crystal-bar filler rod is used. In this case, after annealing the weld, good ductility is achieved. Arc-melted alloys of zirconium and tin can be welded readily. In this case, too, the welds appear to be ductile and corrosion resistant.

In one respect, welding of zirconium is a difficult operation. Because of the rapidity with which zirconium picks up small amounts of nitrogen from the surrounding atmosphere and because of the adverse effect of this nitrogen on the corrosion resistance of the welds, it is necessary that pure zirconium be welded in a closed chamber containing gas of very high purity. The most satisfactory material appears to be Bureau-of-Mines Grade-A helium in which the total contamination, and in particular the nitrogen contamination, is very slight. Welds of crystal-bar zirconium made in this atmosphere have been completely corrosion resistant. Even in the best atmosphere, there are traces of corrosion on the surface of the welds. This corrosion, however, is confined to the surface of the zirconium. Contamination of the welding atmosphere by nitrogen, even to the extent of 100 ppm nitrogen in helium, causes such superficial weld corrosion. Because of its much greater tolerance for nitrogen, it is possible to make corrosion-resistant welds of a Zr:5% Sn alloy in air when a helium-shielded arc is used. Welds made in this manner have been corrosion tested at 600°F in water for thousands of hours without failure.

One unusual characteristic of zirconium is that welds can be made with essentially 100 percent penetration, when fusion occurs only to a depth of perhaps 70 percent of the weld. Solid-phase bonding appears to occur to complete the joining. In those cases where the joint is incomplete, crevice corrosion sometimes occurs in the unbonded portion of the weld. However, this corrosion continues for only a short time during which a superficial film of corrosion product is formed.

Zirconium can also be pressure welded or resistance welded with ease. Completely satisfactory welds can be made readily if contamination is avoided.

MACHINING

The machining characteristics of zirconium resemble those of aluminum. Zirconium is soft and very ductile and galls readily with materials rubbed against it.

Machining practices such as those used for aluminum appear to work quite satisfactorily with zirconium except that cutting speeds must be very low. When zirconium is cut without a coolant, the maximum desirable cutting speed is 50 to 100 surface-ft/min. At higher

speeds, a poor surface finish is obtained. When cutting fluids are used, the allowable speed may be as high as 150 to 200 surface-ft/min. An air jet has been used as a coolant. Tool wear, even with high-speed tools, does not appear to be a serious problem, possibly because the zirconium is so pure that it contains essentially no abrasive inclusions.

Tool angles should be those used to cut aluminum, namely, conventional clearance angles and high-positive rake angles. A rake angle of 30° has been found to work well with all kinds of cutting.

The depth of cut can be that of conventional finishing operations, that is, of the order of 0.020 in. to 0.030 in.

One bothersome characteristic in cutting zirconium is that chips often become rewelded to the surface being cut, giving localized areas where corrosion may occur. This has been more bothersome with very light cuts (0.001-in. to 0.003-in. depth) than with heavier ones.

Zirconium grinds very poorly using ordinary grinding practices. The wheel wear is usually extremely high, and in some cases, a greater volume of wheel material than of zirconium is removed during the grinding operation. To grind zirconium successfully, it is necessary to use a low wheel-speed, 3500 surface-ft/min, with a straight grinding oil and a silicon carbide wheel, shellac bonded. In some work done at Norton Co., it was found that a Norton 37C60-K5V gave best results. Surface finishes of 25 microinches Profilometer reading were obtained. Under these conditions, the wheel wear is low.

HEAT TREATMENT

RECRYSTALLIZATION AND GRAIN GROWTH

As discussed previously, cold-worked zirconium can be annealed at a temperature of 930°F to produce a tensile strength and ductility like those of fully recrystallized material. However, as seen in Fig. 1.24.11, very little grain growth occurs at these temperatures. Appreciable grain growth occurs for normal times of annealing only at temperatures of 1020°F or above.

HYDROGEN EMBRITTLEMENT

In the discussion of impact and aging, it was shown that the amount of hydrogen normally present in zirconium is sufficient to cause embrittlement. Such embrittlement can occur if the hydride phase is dissolved at temperatures of 500° to 700°F and precipitated by slow cooling to room temperature. The embrittlement reveals itself as a considerable loss in impact strength at temperatures below 400°F but not as any significant loss of ductility in a tensile test. The ductility is regained when samples are tested at temperatures at which the hydride phase goes into solution or in samples which have been quenched from such temperatures. In the event that severe forming operations must be performed on zirconium or its alloys and if difficulties are experienced with material as it is normally made, it may be desirable to consider carrying out the fabrication operations either at temperatures of 500° to 700°F or on material which has been quenched from this temperature range.

HEAT TREATMENT OF ALLOYS

Very little is known about the possibilities of improving the strength characteristics of zirconium alloys by heat-treating or aging. It is known that modest increases of hardness and strength occur upon heating crystal-bar zirconium into the beta range. It is also known that tin alloys can be strengthened considerably by quenching from the beta phase. This fact is shown in Table 1.24.4.

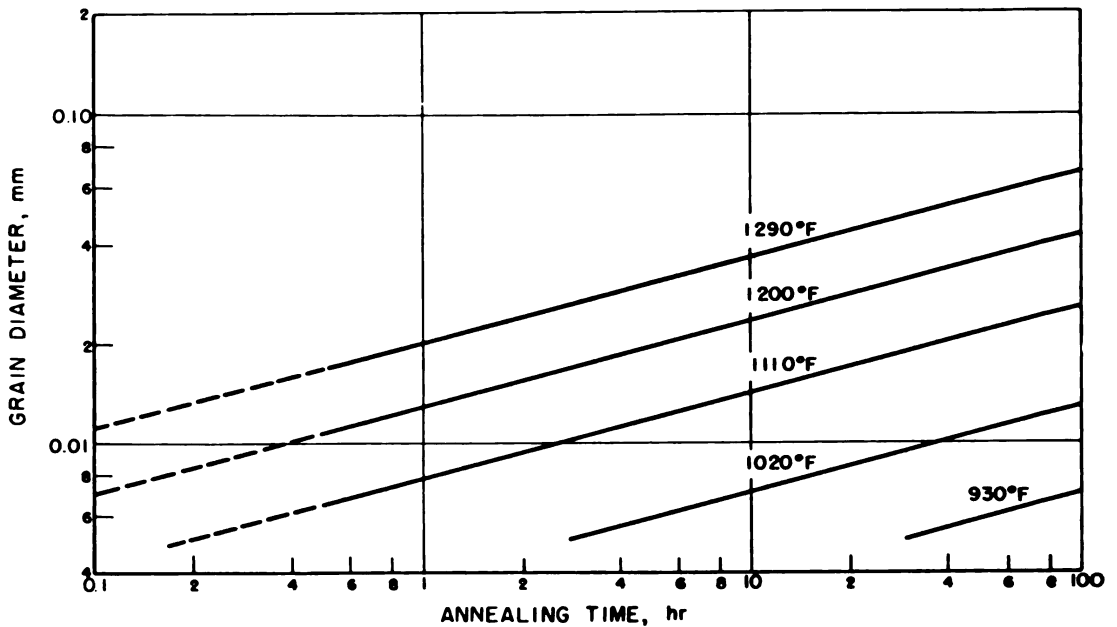


Fig. 1.24.11 — Isothermal Grain-growth Curves for Low-hafnium Foote-iodide Zirconium. Reprinted from N. Davidson, Grain Growth Characteristics of Pure Zirconium, Thesis, University of Pennsylvania, June, 1951. Cold rolled, 50 percent-annealed 1 hr at 1020°F or cold rolled, 80 percent-annealed 1½ hr at 1020°F. Initial grain sizes were 0.0051 and 0.0048 mm, respectively.

Table 1.24.4 — The Tensile Properties of Heat-treated Zirconium-2.5% Tin Alloy
(Progress Report for Month of March, BMI-734, April 1, 1952)

Tensile properties	Thermal treatment	
	Hot-rolled material, cold rolled 40%, annealed 1300°F	Quenched from 1900°F
0.2% offset yield point, lb/sq in.	38,900	64,500
Ultimate tensile strength, lb/sq in.	50,300	80,800
Elongation, %	43	6
Reduction of area, %	61	15

Accompanying this increase in strength, there is, of course, an increase in hardness. This same effect shows up on welding, in which it has been found that the weld bead hardness is 165 Vickers, whereas it is 115 in the unaffected base metal which has been alpha annealed. This increase of hardness is also obtained upon heating in the beta phase and cooling slowly. Material which has been treated in this way has a hardness of 148 Vickers.

TRANSFORMATION KINETICS

There are no published studies of the rate of transformation from alpha to beta or beta to alpha phases. However, it is known that this transformation occurs quite rapidly. For example, even the most drastic quenches do not retain the beta phase in zirconium at room temperatures.

THERMAL CYCLING

Several studies have been made of the effect of thermal cycling on the dimensional stability of zirconium. In general, it has been found that no dimensional changes occurred, although in a few tests, very moderate changes of dimensions have been found. In general, it can be said that zirconium is unaffected by thermal cycling.

CORROSION

One of the most important characteristics of zirconium and its alloys is their corrosion resistance in many media. They are able to resist attack by many acid and alkaline water solutions, by water at elevated temperatures, and by gases at moderate temperatures.

CORROSION BY WATER AND STEAM

Since the first reactor to use zirconium, the STR, is water cooled, its corrosion resistance in water and steam has been studied most thoroughly. In water or steam, temperature has a pronounced effect. Thus, material which resists serious corrosion for a few months in 600°F water may fail in a few weeks in 680°F water, or overnight in 750°F, 1500 lb/sq in. steam.

In the early stages of the corrosion of zirconium, a thin, adherent film of oxide is formed. The thickness of the film gradually increases, then quite suddenly changes in character. For pure zirconium, this deposit is a loose, white powder which can easily be rubbed off. For zirconium-tin alloys, the coating remains adherent, but changes in color from black to tan. In either case, the corrosion rate increases sharply when the character of the film changes.

The corrosion resistance of zirconium in water or steam is extremely sensitive to the amounts of other elements which are present in the zirconium. Certain elements have a very adverse effect on the corrosion resistance, many have no effect, and a few are definitely beneficial.

Early sponge zirconium, graphite melted, was resistant to corrosion by boiling water and by water up to 450°F but was decidedly poor in water at 600°F. The large amounts of carbon and nitrogen present in this material adversely affected its corrosion resistance. Much early crystal bar which was produced was not corrosion resistant in 600°F water. Such material was poor largely because of leaks in the de Boer units which permitted contamination by nitrogen. When very pure zirconium was produced, its corrosion resistance generally was acceptable at 600°F. However, a zirconium specimen may sometimes fail after a long time in 600°F water, even though its composition cannot be differentiated from that of material which continues to have a low corrosion rate for a much longer time.

When those materials which fail after a long time in 600°F water are tested at higher temperatures, the breaks in corrosion rate occur sooner. Testing temperatures of 650° and 680°F have been used to accelerate the detection of such material. Still further acceleration can be obtained by testing in 1500 psi steam at temperatures of 750°F. Although it is not certain that tests in steam at this temperature give results which are completely analogous to those obtained in 600°F water, the same kind of results are generally obtained. An idea of the rate of acceleration which is obtained can be gained from the fact that a

specimen which began to corrode rapidly after 1200 hr in 600°F water showed breakdown in 750°F, 1500-lb/sq in. steam in 18 hr. Other specimens which did not show breaks in their corrosion rate in test times up to 5000 hr in 600°F water maintained a low corrosion rate in this 18-hr test in 750°F steam.

The best zirconium currently being produced will maintain a corrosion rate less than 10 mg/sq dm/mo in a long-time test of several thousand hours' duration. The weight gain initially is a little higher and may be as high as 20 mg/sq dm/mo. Samples which have been tested for 5000 hr have shown an average rate during this time of 5 mg/sq dm/mo. Corrosion is more rapid in 750°F steam. Thus, a particular sample of a 5-percent-tin alloy which had a total corrosion of 20 mg/sq dm in 1600 hr increased in weight by 47 mg/sq dm in 90 hr in 750°F steam at 1500 lb/sq in. Another sample which gained 47 mg/sq dm in 1400 hr in 600°F water gained 63 mg/sq dm in 240 hr in 750°F steam. At still higher temperatures, corrosion was even more rapid. The best material yet tested at a temperature of 900°F in 1500-lb/sq in. steam gained 168 mg/sq dm in 424 hr.

Certain materials are known to be very harmful to the corrosion resistance of zirconium in 600°F water. Zirconium is apparently most sensitive to the effects of nitrogen even in minute amounts. A noticeably detrimental effect occurs when the nitrogen content is 50 ppm, and the material is extremely poor when the nitrogen is 100 to 200 ppm. Other impurities which have an adverse effect include aluminum and titanium. Only a few hundred ppm of either of these materials can be tolerated. Some evidence suggests that silicon and copper may be detrimental. Similarly, carbon has a detrimental effect, although the tolerable amounts have not been defined accurately. Fairly satisfactory results have been obtained with samples containing 500 ppm of carbon, but larger quantities always seem to be detrimental. Even this quantity of carbon probably should be avoided in unalloyed zirconium, if at all possible. The carbide particles themselves are always corroded rapidly.

Most of the materials which might be found as impurities in zirconium, even in amounts of 0.5 to 1 percent, appear to have little effect on corrosion resistance. These include cobalt, molybdenum, tungsten, lead, zinc, thorium, vanadium, beryllium, and oxygen. An element which appears to improve corrosion resistance is tantalum in amounts of 0.1 to 0.3 percent. Another is niobium. Alloying with bismuth has given favorable results.

Tin has a beneficial effect on the corrosion resistance of zirconium, and because tin has a low cross section, it can be used in sizable amounts. If alloyed with zirconium of good corrosion resistance, no benefits are observed; in fact, there is some evidence that the rate of weight gain is somewhat higher than for the tin-free material. However, if tin is added to zirconium of poor corrosion quality, the corrosion resistance can be improved to that of good quality material. It has been shown that tin can overcome the adverse effects of nitrogen, carbon, and aluminum on the corrosion resistance of zirconium.

Thus, it has been found that each percent of tin can overcome the effects of about 300 ppm of nitrogen, and that a 5-percent-tin alloy containing 1500 ppm of nitrogen is corrosion resistant. A 5-percent-tin alloy can be welded in air, using a helium-shielded torch, and retain its corrosion resistance. Similarly, induction-melted alloys made in graphite crucibles were corrosion resistant in spite of a 0.3 to 0.4 percent pickup, when they contained 4-5 percent tin. Other tin alloys have been made from a variety of zirconium-base stocks with poor corrosion resistance, and in every case the tin addition was beneficial.

It has been found that 5 percent of tin is optimum for overcoming the effects of contaminants. However, if the amount of contamination present is small, there is no necessity for a 5 percent tin addition, unless the strength of the high tin alloy is desirable. In fact, there is some evidence that excessive tin additions may be harmful.

The beneficial effects of tin, however, are not universal. Recently, samples of zirconium-tin containing 2.5 percent tin have been found to exhibit breaks in their corrosion rate much as were found with pure zirconium. When rapid corrosion begins on zirconium-tin alloys, the corrosion product is not a loose, white powder, but an adherent, tan film. This type of corrosion product probably has a more adverse effect in a reactor than the

powdery film on pure zirconium because it would not wash off, and would reduce heat transfer considerably.

Evidence is accumulating that iron, nickel, and chromium additions in small amounts prevent this failure, both in tin-free and in tin-containing zirconium.

At temperatures up to 900°F in 1500-lb/sq in. steam, it has been reported that tin does not have a beneficial effect in retarding corrosion. At these temperatures, there is evidence that additions up to 1 percent iron and nickel are helpful in retarding corrosion.

CORROSION BY SOLUTIONS

Table 1.24.5 gives data on the corrosion of iodide zirconium in tests in a number of solutions. Voluminous data on the corrosion of graphite-melted sponge zirconium have been obtained at the College Park Station of the Bureau of Mines. Their reports are the best source of information on this complicated subject.

Crystal-bar zirconium and zirconium-tin alloys successfully withstand attack by uranyl sulfate solution at 250°C.

Table 1.24.5 — Corrosion Data for Iodide Zirconium in Various Liquid Media*

(Zirconium Metal as of 1949, *Journal of Metals*, July 1949, and *Corrosion Handbook*, John Wiley & Sons, 1948)

Media	Concentration, %	Average corrosion rate, mils/yr	
		At 68°F	At 210°F
HCl	5	No attack	No attack
	concentrated	0.1	0.2
H ₂ SO ₄	10	0.2	0.7
	concentrated	...	Attacked
HNO ₃	10	0.01	0.03
	concentrated	0.01	0.05
Aqua regia	...	Slow attack	Attack
HF	...	Rapid attack	...
H ₃ PO ₄	10	0.02	0.05
	concentrated	0.04	Attacked
NaOH	10	No attack†	0.02†
	50	...	0.17†
KOH	10	0.02	No attack
NH ₄ OH	28	0.03	Gained weight
Chlorine water	...	Attacked	Embrittled
FeCl ₃ water	...	Attacked	Embrittled
NaCl	20	...	Slightly tarnished†

*14-day tests, except as noted

† 4 days

CORROSION BY GASES

AIR

Since zirconium reacts with oxygen far more readily than with nitrogen and since the rate of reaction does not appear to be especially affected by oxygen pressure, the rate of

reaction of zirconium with air is essentially the same as with oxygen. Data on the rate of oxidation in air for arc-melted zirconium sponge and an arc-melted Zr:2.5% Sn alloy are given in Fig. 1.24.12. Although the rate of oxidation at normal working temperatures, up to 1450°F, is moderately high, the oxidized material is essentially all on the surface, since there is no appreciable diffusion. Thus, after hot working in air, sandblasting and pickling will remove all of the contaminated material.

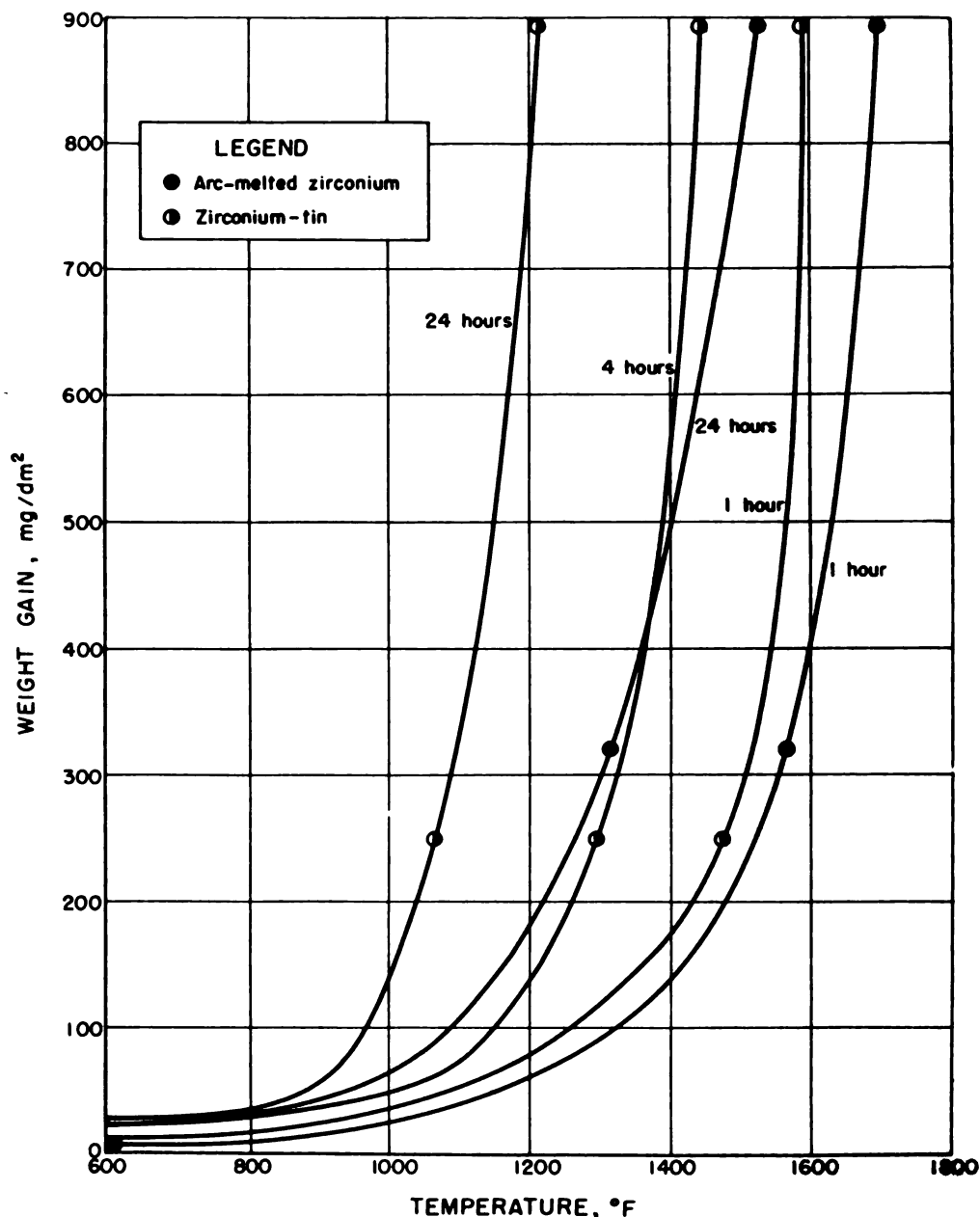


Fig. 1.24.12 — The Rate of Oxidation of Zirconium in an Air Atmosphere. Reprinted from Zirconium Progress Report for the Period of February 15 - March 15, Bureau of Mines, BM-II-21, Mar. 15, 1952.

HYDROGEN

Zirconium will react rapidly with hydrogen once surface films normally present on zirconium are penetrated. Data have been obtained on the rate of reaction between various kinds of zirconium and hydrogen at temperatures in the range of 575° to 850°F. After an initial induction period, which may be as short as one minute or as long as several hours, the rate of reaction has been linear. The order of magnitude of the reaction rate constant at these temperatures is 3 to 8×10^{-3} ml/(cm²/sec).

At low temperatures, the hydrogen pressure in equilibrium with small amounts of hydrogen dissolved in zirconium is very small. The following tabulation gives the pressure of hydrogen gas in equilibrium with 10 ppm of hydrogen in zirconium. These data are extrapolated and may not be precise.

Temperature, °F	Pressure of hydrogen gas in equilibrium with 10 ppm hydrogen in zirconium, mm
600	5×10^{-12}
1000	6.4×10^{-8}
1340	10^{-6}
1470	3.8×10^{-6}
1700	3×10^{-4}
2190	10^{-2}
2550	4×10^{-2}

Hydrogen diffuses through zirconium with amazing speed at low temperatures. In a $\frac{1}{8}$ -in.-diameter cylinder, diffusion is 99 percent complete in 2 hr when the temperature is 600°F. Variation of the diffusion constant as a function of temperature is given in Fig. 1.24.13.

In spite of the speed of hydrogen diffusion in zirconium, diffusion can be a limiting factor in the preparation of zirconium dihydride for powder metallurgy. If sponge zirconium or material of large surface area is heated in hydrogen at 750°F, reaction with hydrogen is rapid, and conversion to hydride is complete in a few hours. Massive crystal bars of zirconium, however, must be heated for 20 hr at 1470°F for complete conversion.

OXYGEN

Oxygen reacts rapidly with zirconium at all temperatures. At low temperatures, the oxide film formed is protective, and further oxidation in significant amounts does not occur. At elevated temperatures, oxidation continues. The amount of oxygen reacted with zirconium specimens at various temperatures exposed to oxygen at one atmosphere is given in Fig. 1.24.14. The rate of oxidation does not appear to be affected significantly by oxygen pressure; other results at an oxygen pressure of 0.1 atm are nearly the same as these.

Oxygen is known to diffuse rapidly through zirconium. However, numerical data on diffusion rates are not available because of the difficulty of making oxygen analyses. Qualitative data show that a strong metallic bond can be obtained between two pieces of zirconium at a temperature as low as 1400°F, suggesting that both oxide and nitride layers must have diffused sufficiently at this temperature in an hour or two for the surface to be metallic. On the other hand, diffusion is not so rapid that processing of zirconium and its alloys in air is not permissible. Except in large sections, such as forgings, such processing probably should be done in the alpha phase where diffusion is slower. With normal processing times in the alpha phase, the contaminated layer is less than a mil in depth.

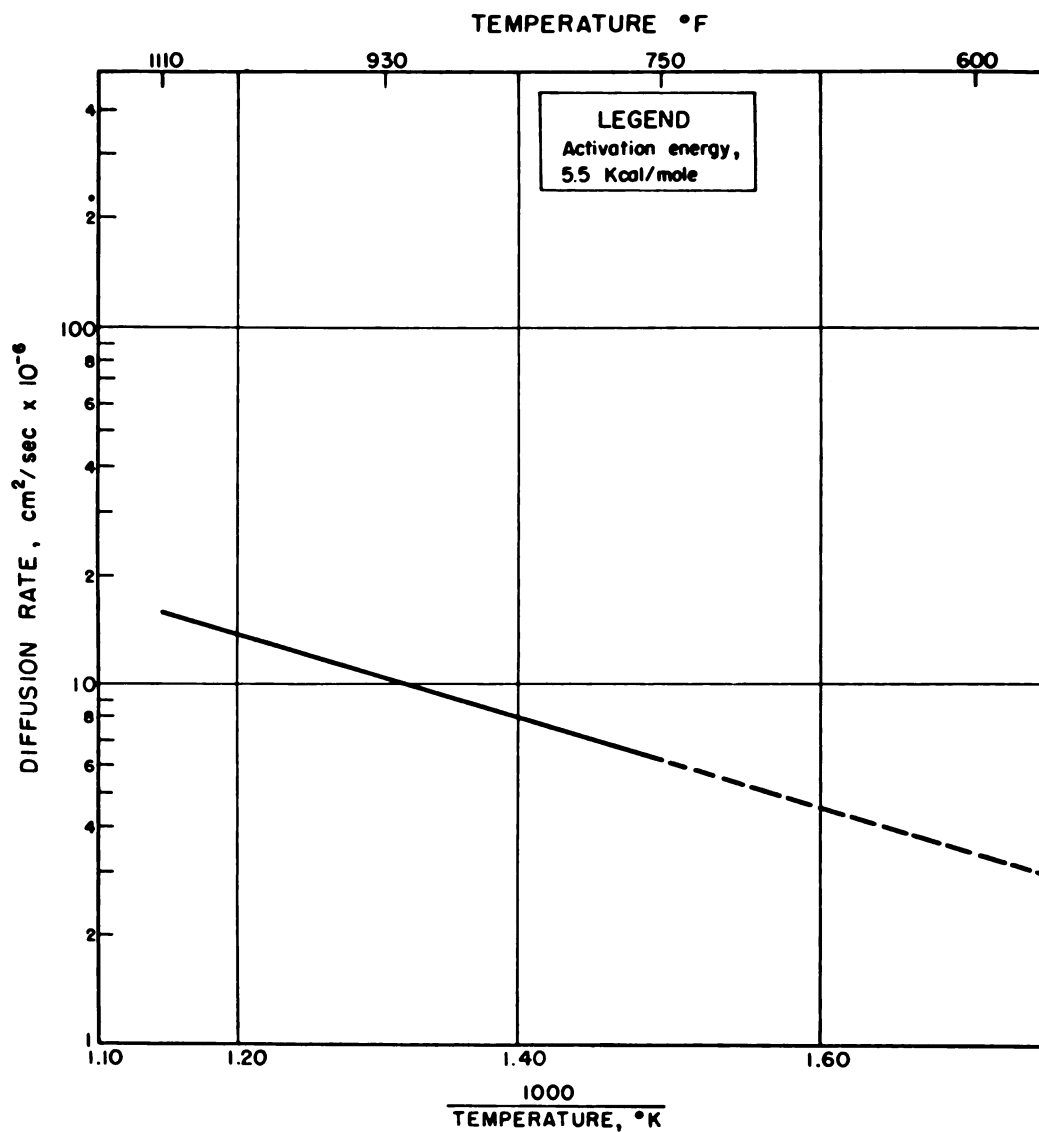


Fig. 1.24.13 — Diffusion Coefficient of Hydrogen in Zirconium. Reprinted from R. W. Dayton, et al, Hydrogen Embrittlement of Zirconium, BMI-767, Aug. 22, 1952.

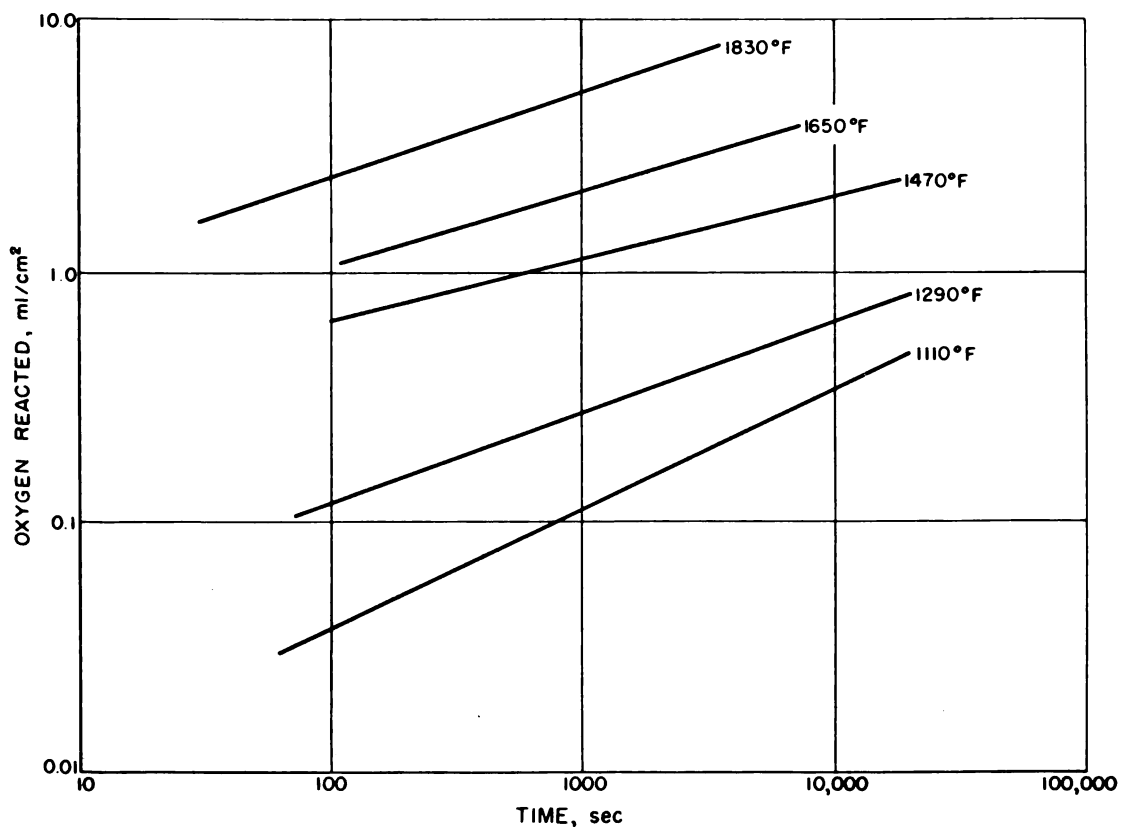


Fig. 1.24.14 — The Amount of Oxygen Reacted With Zirconium Specimens at Various Temperatures. Reprinted from M. W. Mallett, et al, The Reaction of Zirconium Metal Surfaces With Oxygen, BMI-727, Feb. 25, 1952. Oxygen pressure, 1 atm.

NITROGEN

Zirconium does not react with nitrogen at temperatures as low as it does with oxygen. Studies have been made of the nitrogen-zirconium reaction in the temperature range of 1000°-1400°C at 1 atm pressure, using pure zirconium and zirconium-tin alloys with 2, 3, and 5 percent tin. The data show that the reaction follows a parabolic law for the zirconium-tin alloys as well as for the pure zirconium. The parabolic rate constants and the energies of activation are given below.

Tin in Alloy, %	Parabolic Rate Constant, cm ² /sec	Activation Energy, kcal/mole
0 (Pure Zr)	$8.30 \times 10^4 e^{-54}$, 000/RT	54.0 ± 3.4
2	$1.22 \times 10^5 e^{-63}$, 400/RT	53.4 ± 1.5
3	$2.63 \times 10^5 e^{-64}$, 700/RT	54.7 ± 5.5
5	$2.52 \times 10^4 e^{-60}$, 300/RT	50.3 ± 1.9

The reaction rates for nitrogen with low-hafnium zirconium and zirconium-tin alloys at various temperatures are given in Fig. 1.24.15.

Other data on the reaction rate of a sponge Zr : 2.5% Sn alloy with nitrogen are given in Table 1.24.6.

The diffusion constant for nitrogen in zirconium as a function of temperature is given in Fig. 1.24.16.

CORROSION BY LIQUID METALS

The following behavior of zirconium in various liquid metals has been observed:

Gallium - 840°F, bad attack
 Mercury - 200°F, good; 400°F, fair resistance
 Lithium - 1830°F, ZrN tarnish film, 4 hr
 Sodium-Potassium - 1110°F; negligible weight gain, 6 days
 Lead - 1830°F, Sn - 930°F; Pb-Bi-Sn - 930°F; resistant
 Bismuth - 1830°F, severe attack
 Magnesium - 1200°F, bad attack
 Calcium - 2370°F, resistant

In tests (at 930°F in filtered sodium) of alloys containing 0 to 3 percent of tin, all gained weight at the rate of 65 mg/dm²/mo.

CORROSION BY FUSED SALTS

Essentially no data are available on the corrosion of zirconium by fused salts. In a single 24-hr test in sodium hydroxide, no significant corrosion of zirconium was observed at 1000°F. At a temperature of 1500°F, attack was extremely severe in 24 hr. Mixtures of alkali fluorides attacked zirconium badly at 1500°F.

PICKLING

All pickle baths which attack zirconium include hydrofluoric acid, since zirconium resists attack by almost all other acids. Several bath compositions have been tested, and satisfactory results have been obtained with a solution containing 50 ml of concentrated nitric acid and 50 ml of water to which has been added 3 or 6 gm of ammonium fluoride per 100 ml of solution. This bath is used at room temperature and removes metal at the rate of 0.0005 in./min for the 3-gm bath, or 0.001 in./min for the 6-gm bath. The 3-gm

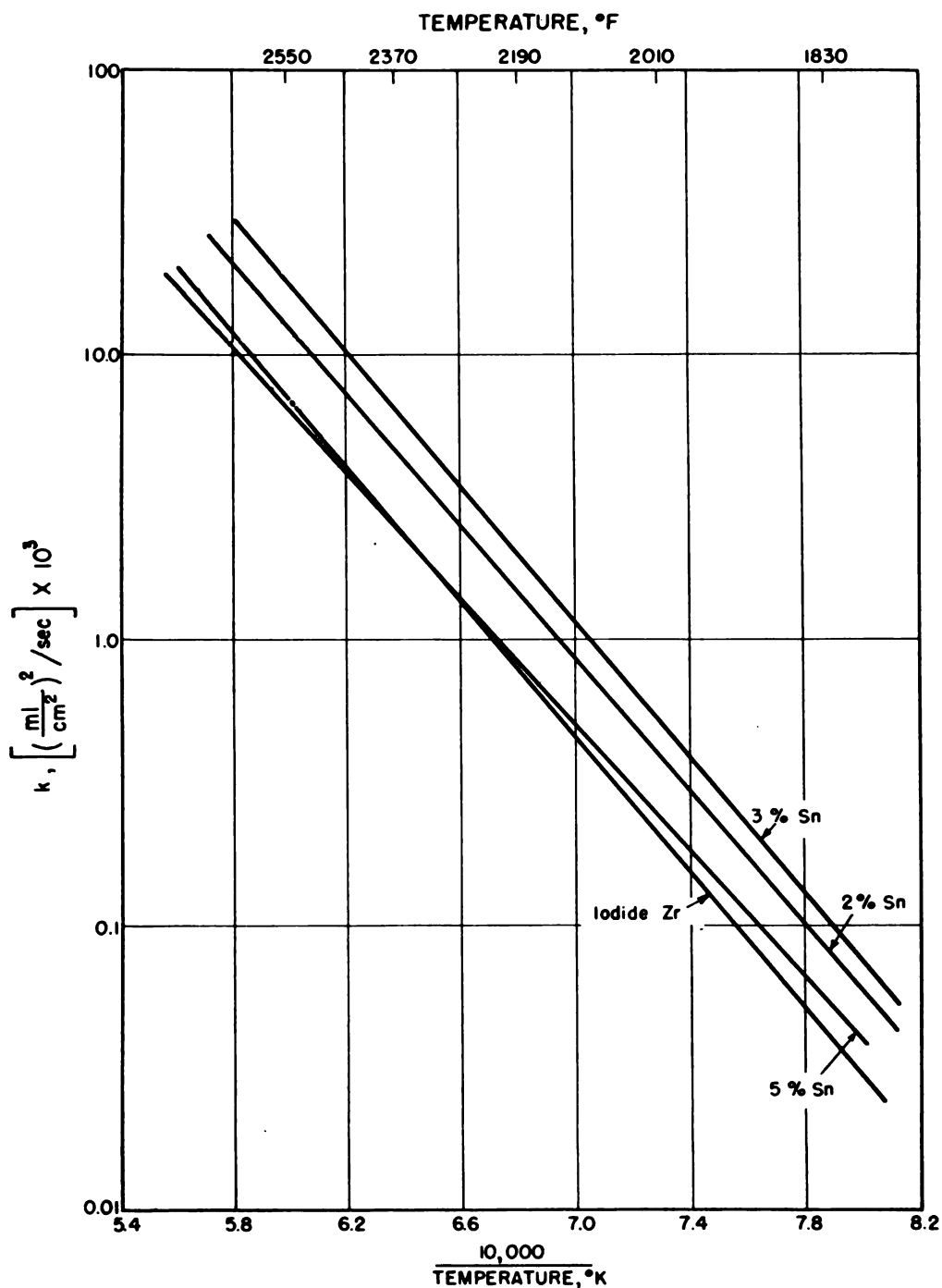


Fig. 1.24.15 — The Reaction Rates for Nitrogen With Arc-melted, Low-hafnium Zirconium and Zirconium-tin Alloys at Various Temperatures. Prepared from data of Battelle Memorial Institute, Nov. 1, 1952.

**Table 1.24.6 — Reaction of Nitrogen With Zirconium-
2.5% Tin at Various Temperatures**

(Zirconium Progress Report for the period
February 15 - March 15, BM-II-21, Mar. 15, 1952)

Temperature, °F	Weight gain, mg/sq dm	
	1-hr heating	24-hr heating
1110	1.3	...
1290	3.1	...
1470	8.6	18
1650	10	48
1780	17	74

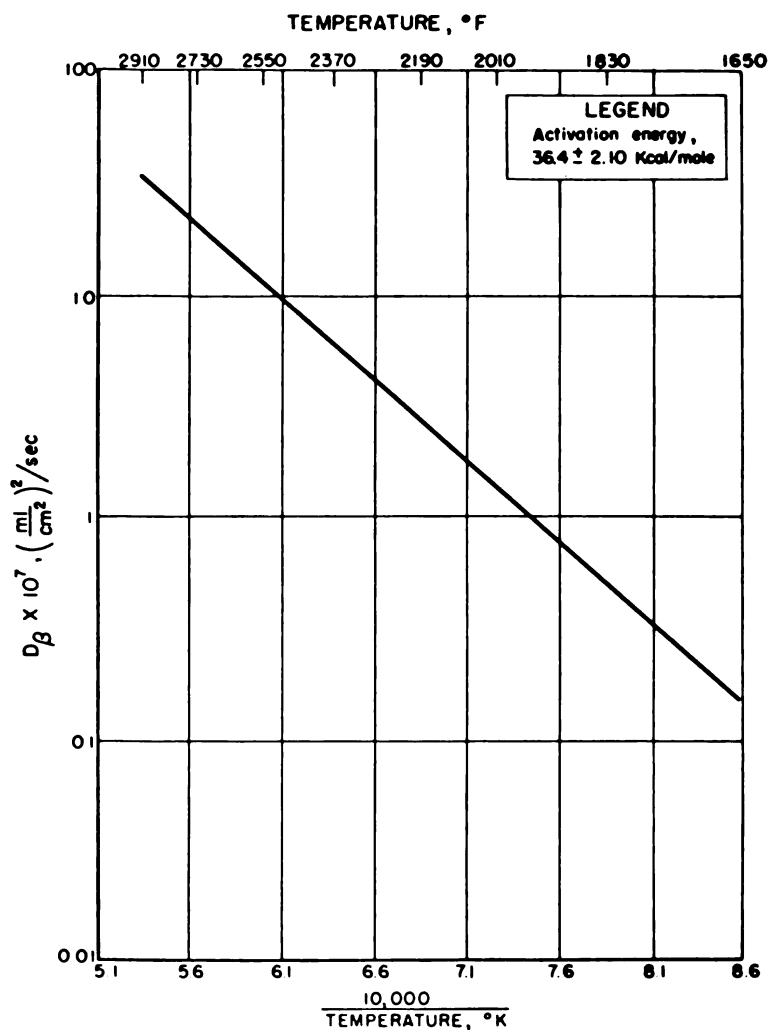


Fig. 1.24.16 — The Variation of the Nitrogen Diffusion Coefficient With Temperature. Reprinted from M. W. Mallett, et al, *The Surface Reaction of Nitrogen with Beta Zirconium and the Diffusion of Nitrogen in the Metal*, BMI-709, Dec. 12, 1951.

bath is preferred, since gas evolution is less violent. The articles which have been pickled must be washed thoroughly when removed from the bath, especially if crevices are present. Some difficulties have been experienced when corrosion tests follow pickling of a sample containing crevices. It would appear that traces of the pickling composition are trapped in the crevices and promote corrosion in their vicinity. Very thorough washing and neutralizing will eliminate such difficulties.

PROTECTIVE COATINGS FOR ZIRCONIUM

For some applications, it would be desirable to be able to coat zirconium with thin layers of other metals which possess special characteristics lacking in zirconium. Thus, a stainless steel or nickel coating would be desirable for protection against corrosion at temperatures higher than can be used with pure zirconium or its alloys. Similarly, chromium plating would be desirable for applications in which good frictional characteristics were desirable. Unfortunately, the characteristics of zirconium are such that no outstanding coating method of any sort has yet been found. Zirconium appears to form brittle layers of intermetallic compounds with essentially all of the common metals. For this reason, the coatings are apt to be nonadherent.

CLADDING

Attempts have been made to clad zirconium with nickel, Monel, Inconel, titanium, and an 18-8 stainless steel by rolling. All of these metals except titanium formed compounds at the zirconium interface, and the resulting bonds had poor mechanical properties. The titanium-zirconium bond had good strength and ductility and showed no tendency to crack during thermal cycling. However, such clads will not greatly extend the utility of zirconium, since the characteristics of titanium are similar to those of zirconium in most respects. However, titanium does appear to have slightly greater resistance to corrosion by water and might be usable in some special applications. It should also be remarked that some of the low titanium alloys of zirconium, which would be present in the diffusion bond, have very poor corrosion resistance.

An investigation has been made also of diffusion couples of zirconium and copper, molybdenum, platinum, silver, and tantalum. This work indicated that all of these materials form hard, brittle diffusion products with zirconium. For that reason, they offer no promise.

ELECTROPLATING

It has been possible to make strong bonds between zirconium and electro-deposited nickel and iron. The procedure followed is to use a particular etching procedure which provides mechanical keying of the electro-deposit and to follow this with an annealing treatment which produces a diffusion bond. The time and temperature must be regulated so that the thickness of the intermetallic compound layer is not excessive. In this way, bonds can be obtained which have a strength of 55,000 lb/sq in. for nickel and 40,000 lb/sq in. for iron.

METALLOGRAPHY

There are no unusual difficulties in preparing metallographic specimens of zirconium other than those encountered with any specimen of a soft, ductile material. Ordinary grind-

ing and polishing operations have been used with sapphire dust, zirconium oxide, and tin oxide as the abrasives for the final polishing. Chemical polishing methods have been used successfully. After grinding on 2/0 paper, the specimens are immersed in a solution containing 40 percent water, 45 percent concentrated nitric acid, and 8 to 15 percent of 48-percent hydrofluoric acid. After 10 to 30 sec treatment, the specimens are washed in cold water.

For final etching, a 10-percent solution of ammonium bifluoride in distilled water has been used. Another etchant is composed of: 60 ml 30-percent hydrogen peroxide, 30 ml concentrated HNO_3 , 20 ml ethyl alcohol, and 2 drops 48-percent HF. Still another contains $\frac{1}{2}$ to 1 ml of 48-percent HF, 0 to 2 ml HNO_3 , 0 to 15 ml H_2O , and 6 ml of glycerine.

For the study of inclusions, a modified aqua regia has been used. This consists of: 10 - 15 ml HNO_3 , 40 ml HCl , and 3 drops HF. Several kinds of nonmetallic inclusions which often appear in zirconium have been tentatively identified under the microscope. The following information on these inclusions has been obtained.

ZIRCONIUM CARBIDES

Carbides occur as broken stringers or as spheroids which appear isotropic under polarized light. The carbide etches to a light-gray color with the modified aqua regia solution (containing hydrofluoric acid) or the ammonium bifluoride etchants. Heat treatments in the high-alpha and low-beta ranges have little effect on the size of the particles.

ZIRCONIUM HYDRIDES

The "spiny" rough-edged inclusion which is frequently observed in iodide zirconium is believed to be a hydride. The inclusion is found as continuous stringers, which polish in slight relief and appear isotropic when examined by polarized light.

ZIRCONIUM NITRIDES

No inclusion has been generally agreed to be the nitride. Some investigators believe that nitrogen-rich areas in iodide zirconium can be identified. These areas appear as "bands" which stain slightly when the polished metal is etched with ammonium bifluoride. The areas attacked in etching are the same areas attacked by corrosion in tests made in 600°F water. Other investigators claim to have identified a nitride phase along grain boundaries.

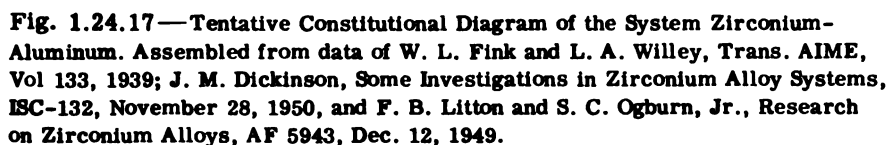
ZIRCONIUM OXIDES

The inclusion believed to be the oxide or a high oxygen phase occurs not only within the grains but also along grain boundaries. The inclusion appears as discrete particles in iodide zirconium as arc melted, as alpha annealed, or as quenched from temperatures in the high-alpha range. In beta-quenched material, the masking effect caused by the "Widmānstatten-like" structure makes recognition of the inclusions very difficult.

ZIRCONIUM ALLOYS

ZIRCONIUM-ALUMINUM

The constitutional diagram for zirconium-aluminum alloys, which is known only incompletely, is shown in Fig. 1.24.17. This diagram shows appreciable aluminum solubility in the beta phase but only slight solubility in the alpha phase.



A tentative constitutional diagram for alloys of carbon and zirconium is given in Fig. 1.24.18. Carbon as an alloying material does not form desirable alloys with zirconium. The diagram has importance, because when zirconium is melted in a graphite crucible, carbon contamination occurs. This contamination is detrimental to corrosion properties of high-temperature water, but has no marked effect on mechanical properties after the cast structure has been broken up by forging.

The constitutional diagram for these alloys is given in Fig. 1.24.19.

The constitutional diagram for zirconium and iron alloys is shown in Fig. 1.24.20.

Owing to the importance of hydrogen in causing embrittlement in zirconium, it would be desirable to report the zirconium-hydrogen constitutional diagram. However, the data

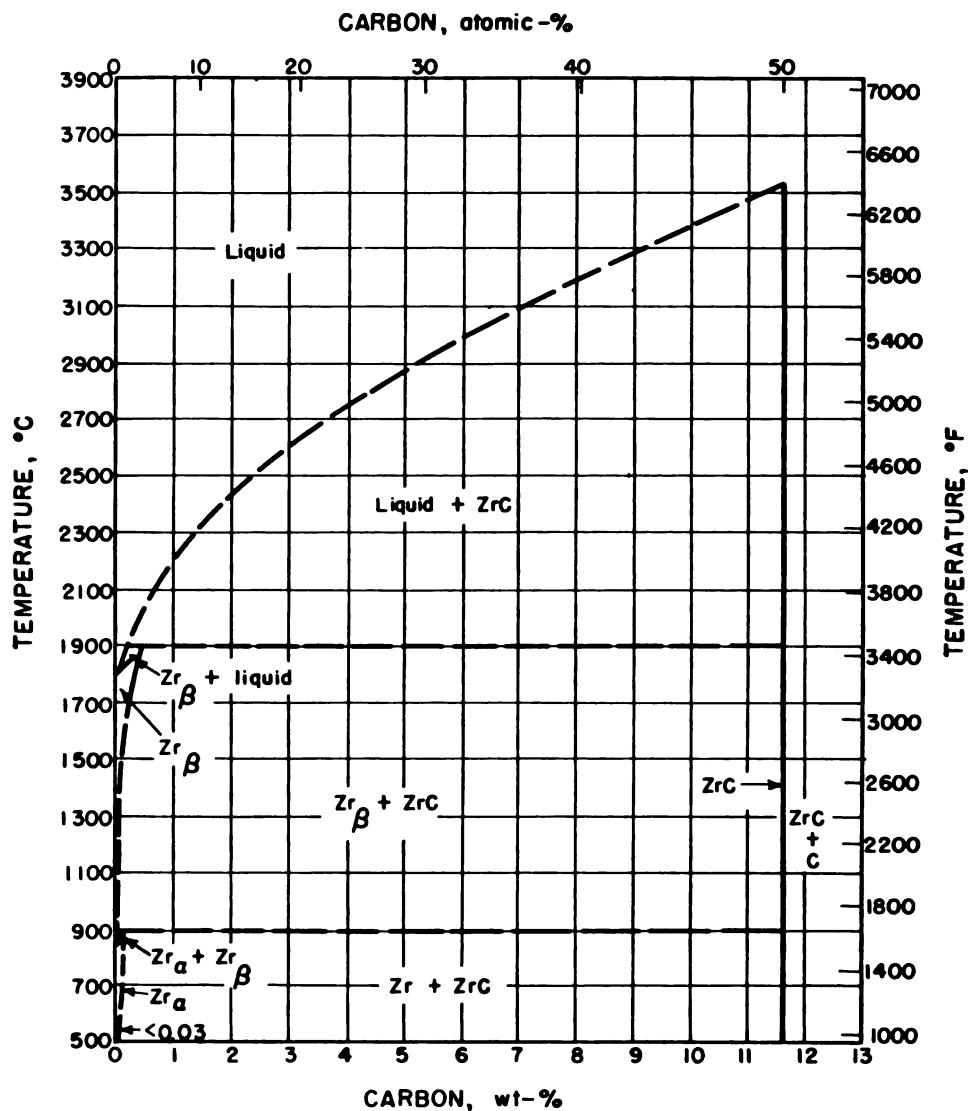
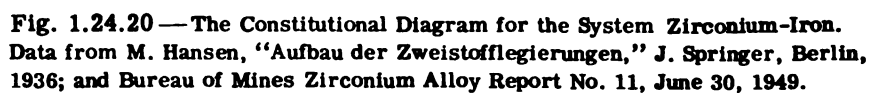
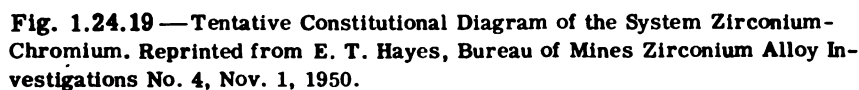


Fig. 1.24.18—Tentative Constitutional Diagram of the System Zirconium-Carbon. Prepared from data of P. Chiotti, *Some Investigations into Zirconium Alloy Systems*, ISC-132, November 28, 1950, and M. W. Mallett, in Progress Report for Month of January, 1951, BMI-56, Feb. 1, 1951.



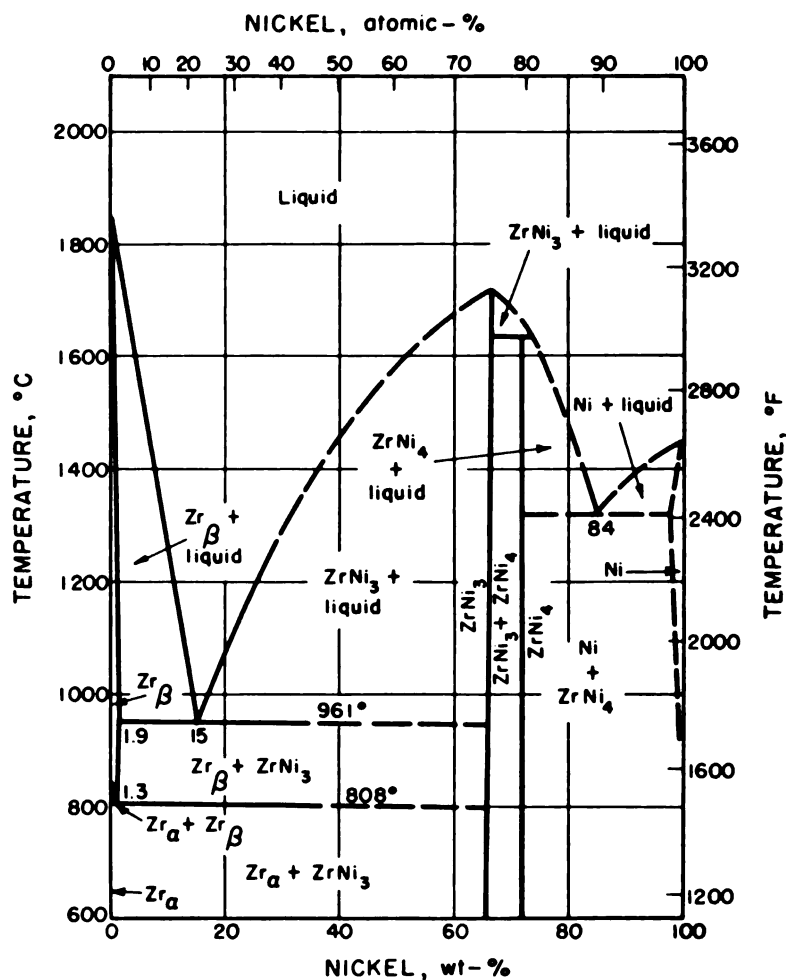


Fig. 1.24.21 — Tentative Constitutional Diagram for the System Zirconium-Nickel. Data taken from M. Hansen, "Aufbau der Zweistofflegierungen," J. Springer, Berlin, 1936; and E. T. Hayes Bureau of Mines Zirconium Alloy Reports Nos. 5 and 11, Jan. 1, 1951 and Jan. 1, 1952.

currently available are too scattered and incomplete to permit a useful diagram to be given. The range of hydrogen content which is important in the application of zirconium is up to 0.02 percent. The solid solubility of hydrogen in alpha zirconium has been reported to be 0.03 percent hydrogen at 750°F and about 0.07 percent at 1110°F. This value appears to be fairly consistent with data obtained on aging, which showed that aging can be obtained with samples containing 40 ppm hydrogen, owing to precipitation of the hydride phase at temperatures below 570°F.

ZIRCONIUM-NICKEL

The constitutional diagram for these alloys is shown in Fig. 1.24.21.

ZIRCONIUM-NITROGEN

Insufficient data have been reported to permit the constitutional diagram for this system to be given. Data are reported on solubility of nitrogen in beta zirconium based on results obtained in diffusion experiments. These data are given in Table 1.24.7.

Table 1.24.7—Solubility of Nitrogen in Zirconium, Based on Diffusion Experiments

Temperature, °F	Solubility of nitrogen	
	Weight-%	Atomic-%
1650	0.02	0.13
1830	.07	.45
2010	.16	1.03
2190	.27	1.73
2370	.35	2.24
2550	.45	2.85

ZIRCONIUM-OXYGEN

Oxygen is a normal impurity in zirconium. In crystal-bar zirconium, the oxygen content is not over a few hundred ppm and has a rather small effect. In sponge zirconium, the oxygen content may be from 600 to 1000 ppm and has a significant effect on both hardness and transformation temperature. The effect of the oxygen on hardness has been discussed previously. The effect on transformation temperatures is shown in Fig. 1.24.22. As may be seen in this diagram, the transformation range of zirconium is greatly spread out by additions of oxygen. The upper transformation temperature is increased greatly, perhaps 100°F, for 0.1 percent oxygen, but the lower transformation temperature is hardly changed.

ZIRCONIUM-THORIUM

The constitutional diagram for alloys of zirconium and thorium is given in Fig. 1.24.23. There appears to be complete intersolubility between beta zirconium and some high-temperature thorium phase. Alpha zirconium is soluble in thorium to the extent of about 5 percent, but there is essentially no solubility of thorium in alpha zirconium.

ZIRCONIUM-TIN

The constitutional diagram for zirconium-tin alloys, according to present concepts, is given in Fig. 1.24.24. Most of the work on this diagram has been done on low-tin alloys. Since the best engineering properties and corrosion properties of these alloys are found in the range of 0 to 5 or 10 percent of tin, it can be considered that the important features of the diagram are known moderately well. Two features of this diagram are especially important.

The first is the transformation temperature. This transformation, which occurs at slightly under 1600°F for pure zirconium, is raised approximately 100°F by an addition of 2.5 percent tin. When sponge alloys are being considered, the nonmetallic contaminants can be expected to raise the transformation temperature by another 100°. Thus, for a sponge Zr : 2.5% Sn alloy, the transformation temperature will be approximately 1800°F.

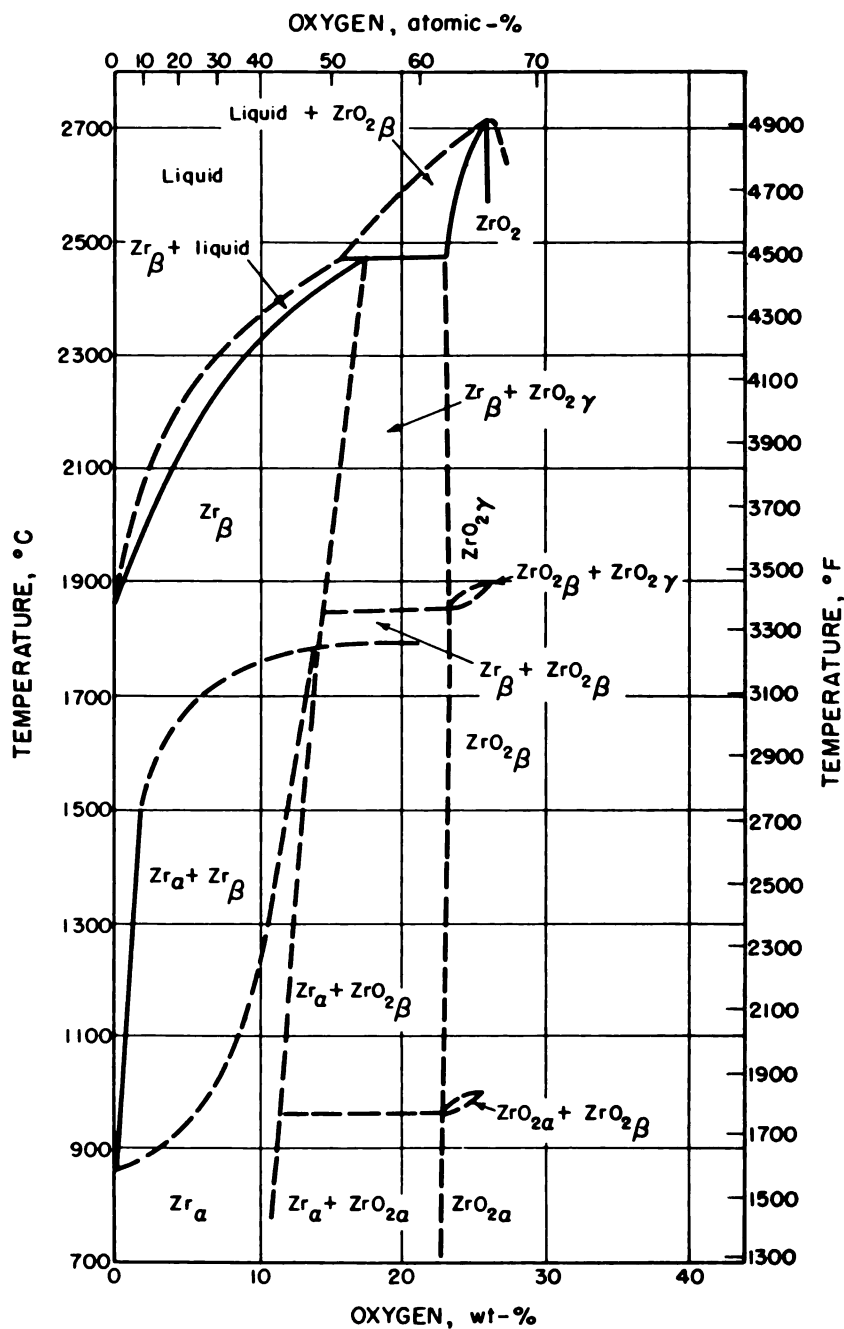


Fig. 1.24.22—Tentative Constitutional Diagram of the System Zirconium-Oxygen. Constructed from data of D. Cubicciotti, Illinois Institute of Technology, Report No. 6 to ONR, May 1952; J. H. de Boer and J. D. Fast, *Recueil des travaux chimique des Pays-Bas*, Vol 55, 1936; and C. S. Harman et al, *Properties of Solid Oxides*, NEPA-808 BMI-20, June 1948.

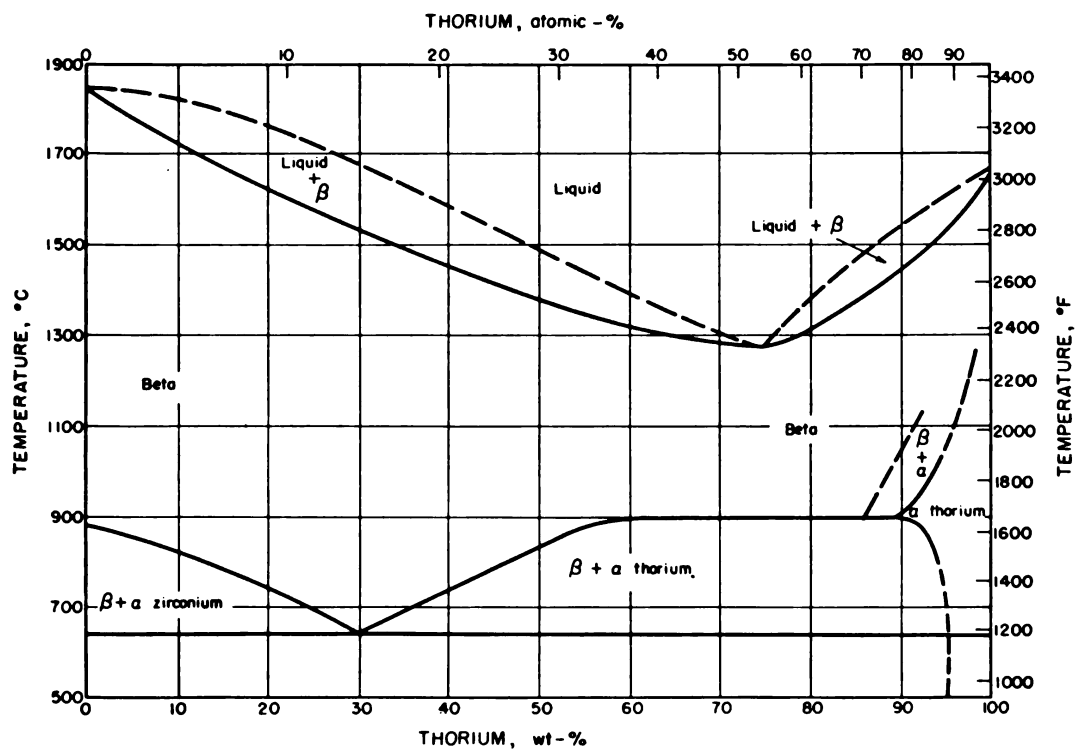


Fig. 1.24.23 — The Constitutional Diagram of the System Zirconium-Thorium. Reprinted from O. N. Carlson, Some Studies on the Uranium-Thorium-Zirconium Ternary Alloy System, ISC-102, June 5, 1950.

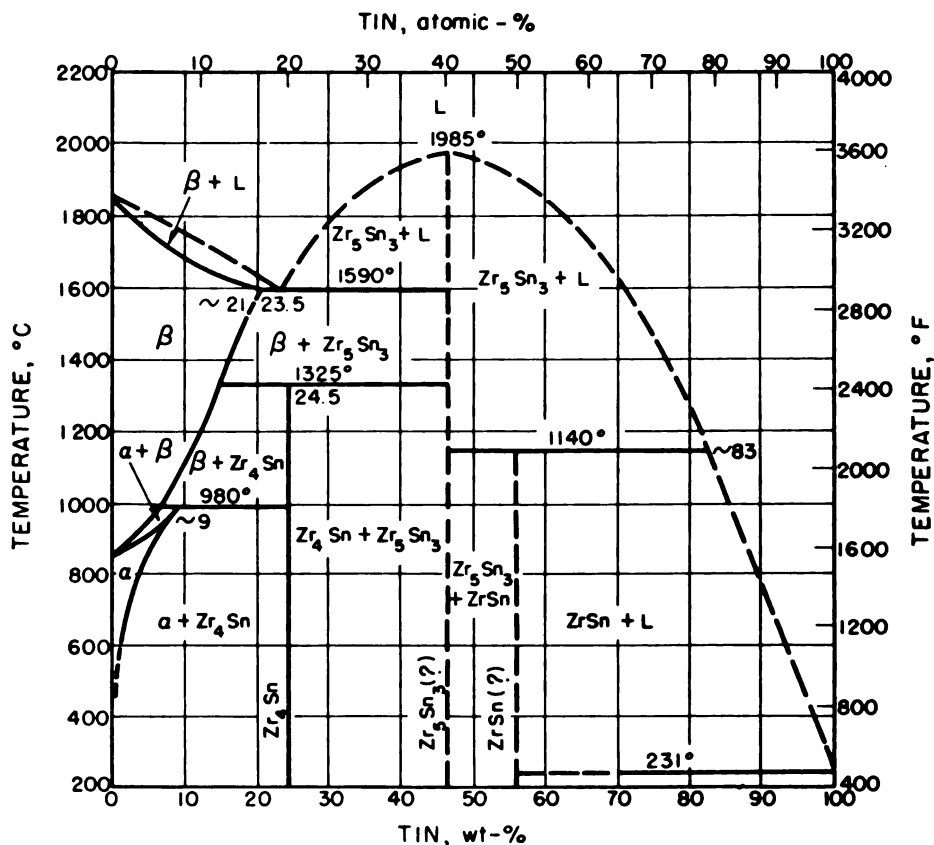


Fig. 1.24.24 — The Constitutional Diagram of the System Zirconium-Tin.
 Reprinted from Phase Diagrams of Zirconium-base Binary Alloys, Armour
 Research Foundation of Illinois Institute of Technology, COO-89, April 14, 1952.

This temperature is important because it has been found that little grain growth occurs in the alpha phase, whereas large grains are invariably grown in the beta phase.

A second important feature of the constitutional diagram is the solid solubility of tin in alpha zirconium. This solubility line has not yet been determined with high accuracy owing to the difficulty of precipitating and identifying the tin-rich phase. The best estimates at the present time are that at a temperature of 1300°F, 2 to 3 percent of tin can be dissolved. At lower temperatures, the only data have been obtained by Westinghouse, using the appearance of a true yield point as an indication of supersaturation. With a 1-percent-tin alloy, strain aging was found at temperatures below 750°F but not at temperatures above this. This suggests that the solubility of tin at this temperature may be approximately 1 percent. The shape of the solubility line for tin in alpha zirconium is such as to suggest that aging of these alloys might occur. Such aging has not, however, been found, although work on the subject is continuing.

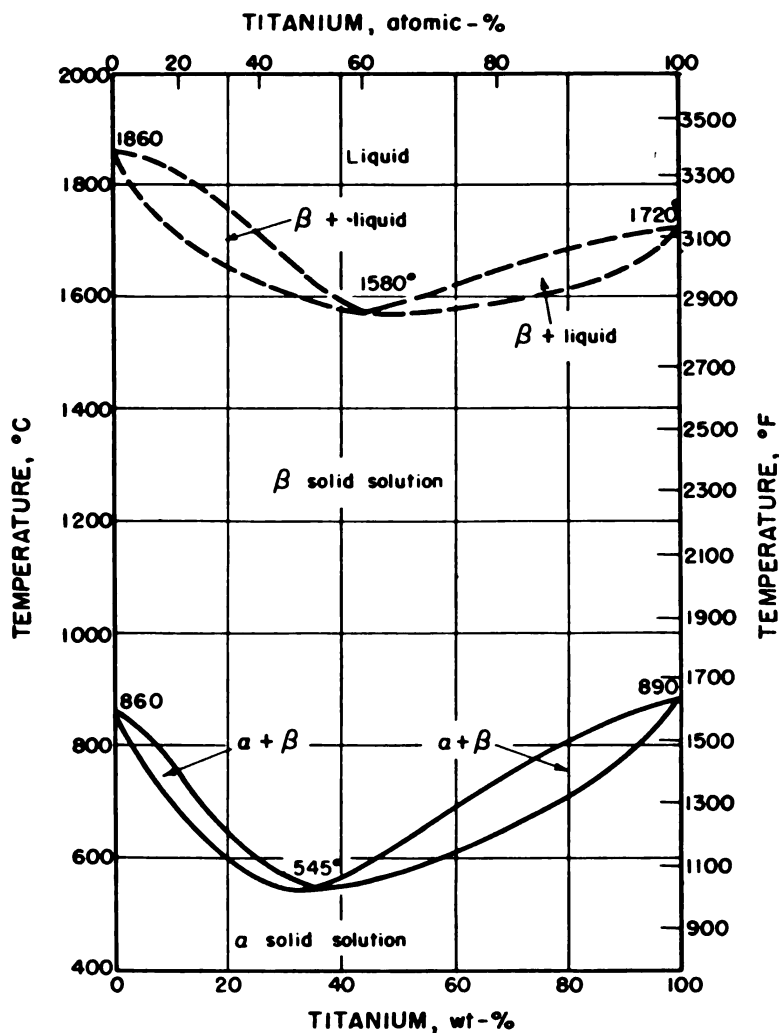


Fig. 1.24.25 — The Constitutional Diagram for the System Zirconium-Titanium. Reprinted from J. D. Fast, *Recueil des travaux chimique des Pays-Bas*, Vol 58, 1939.

ZIRCONIUM-TITANIUM

The constitutional diagram for zirconium-titanium alloys shown in Fig. 1.24.25 shows that there is a continuous series of solid solutions in both the alpha and beta phases. There is a minimum in both the alpha to beta transformation line and in the solidus line.

ZIRCONIUM-URANIUM

The constitutional diagram for the system zirconium-uranium is given in Chap. 1.22. (Fig. 1.22.40).

The diffusion constants were determined for the zirconium-uranium system, using a 14 weight-percent uranium-zirconium alloy coupled to zirconium. It was found that the alpha-beta zirconium transformation temperature, 1585°F, provided a natural division for the diffusion characteristics. The diffusion in the beta range can be described by the relation:

$$D = 0.46 \exp (-47,300/RT) \text{ cm}^2/\text{sec}$$

and the diffusion in the alpha range by the relation:

$$D = 3.75 \times 10^{-6} \exp (-15,000/RT) \text{ cm}^2/\text{sec}$$

The diffusion constants for the alpha range are abnormally low, and perhaps when the zirconium-uranium equilibrium diagram is known, further analysis may provide a more reasonable relation.

The use of the Dushman-Langmuir relation for calculating the activation energy in the cubic beta range provided an excellent check of 47,000 cal/mole with the experimental value of 47,300 cal/mole.

SELECTED READING LIST*

Battelle Memorial Institute, Murray C. Udy, Homer L. Shaw and Francis W. Boulger, BMI-711, February 20, 1952 (classified).

Battelle Memorial Institute, Murray C. Udy and Francis W. Boulger, BMI-T-50, June 15, 1951 (classified).

Battelle Memorial Institute, Murray C. Udy and Francis W. Boulger, BMI-T-49, March 20, 1951 (classified).

Battelle Memorial Institute, Murray C. Udy and Francis W. Boulger, BMI-T-48, December 29, 1950 (classified).

Battelle Memorial Institute, Murray C. Udy and Francis W. Boulger, BMI-T-47, November 17, 1950 (classified).

*These reports summarized the available data as of 1951. Data on zirconium and its alloys have been accumulated rapidly since these reports were issued, but the information has not been assembled in readily accessible reports. The more recent information can be obtained by reading the progress reports of installations which are working on zirconium. These include Ames, Argonne National Laboratory, Battelle Memorial Institute, Bureau of Mines, Massachusetts Institute of Technology, Sylvania Electric Products Company, and Westinghouse Atomic Power Division.

CHAPTER 1.25

High-cross-section Materials

M. C. Udy

REACTOR APPLICATION

Because of their relatively high thermal-neutron-absorption cross sections, the most likely use of the materials discussed in this chapter is in control applications. Boron and boron-containing materials, cadmium, cobalt, hafnium, mercury, rhodium, and silver, discussed below, have already received some attention within the project. A number of potentially useful elements and compounds of lesser cross section are not covered; of these, gold and indium are well known metallurgically and chemically, while iridium is of little interest because of its scarcity. Some rare-earth elements of extremely high cross section (Chap. 1.16) are of interest for control applications.

Alloys containing elements of high cross section offer combinations of nuclear properties, particularly with resonance peaks, that are useful in thermal reactors. Data for some representative alloys of this type are included in this chapter.

ABUNDANCE AND AVAILABILITY

BORON

The earth's crust is estimated to contain about 0.001 percent boron. Commercially, boron is obtained from deposits of ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$), colemanite ($\text{CaB}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), and rasorite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$) in the desert regions of California.

It has been estimated that the isotope B^{10} , which accounts for the high cross section of boron, can be produced as amorphous boron in ton lots for about \$60/lb. This compares with a price of \$15/lb for amorphous natural boron. Crystalline boron in large lots costs about \$150/lb. Boron carbide costs from \$4.50 to \$7.50/lb, depending on the grade.

Table 1.25.1 lists some properties of various boron-containing materials.

CADMIUM

Cadmium is estimated to exist in the earth's crust to the extent of about 0.0005 percent. The only cadmium mineral of any importance is greenockite (CdS). Even this mineral is not found in deposits of any size or commercial value. The world's output of cadmium is obtained largely from the residues of electrolytic zinc, retort zinc, and lithopone plants. These sources are supplemented by the fumes from lead and copper smelters.

World production in 1949 was 5600 tons; the May 1952 price was \$2.55/lb.

Table 1.25.1—Properties of Various Boron Vehicles
 ("Construction of Cheap Shields, a Survey," ORNL-243, Jan. 16, 1950)

Material	Boron		Density, gm/cm ³	Other Elements, gm/cm ³
	gm/cm ³	%		
Crystalline B, theoretical density and purity	2.33	100	2.33	...
Crystalline B, hot pressed with B ₂ O ₃	2.00	98 max	2.04	...
Amorphous B, hot pressed with B ₂ O ₃	1.8	80	2.3	Mg and C impurities
B ₄ C, Norton Abrasive Grade	2.0	80	2.5	<1% impurities
B ₄ C, Norton Metallurgical Grade	1.8	78	2.3	Some Fe and C
B ₁₀ H ₁₄ (a paraffin-like material)	0.83	88.4	0.94	0.108 H ₂
Boral (¼-in. sheet and Al wrapper)	1.012	40	2.5	1.3 Al, 0.25 C
Boroxal (¼-in. sheet and Al wrapper)	0.305	15	2.0	1.0 Al, 0.70 O ₂
B ₂ O ₃	.575	31	1.85	1.30 O ₂
Colemanite	.0606	16	2.3	0.056 H ₂
Ammonium pentaborate	(.40)	20	(2)	.074 H ₂
Borax	.197	11.4	1.73	.092 H ₂
Boroffin (20% B ₂ O ₃)	.062	6.2	1.0	.089 H ₂
Sat'd H ₃ BO ₃ soln in H ₂ O (3%)	.0093	0.93	1.0	.119 H ₂
M1 cement (magnesium oxy-chloride plus colemanite)	.0845	4.45	1.90	.072 H ₂
Ferroboration	(1.0)	~20	(5.0)	Fe and C
Boron steel	(0.152)	~2.0	(7.6)	Fe, C, and Mn
Lead borate glass (assumed 60% PbB ₂ O ₄ 40% B ₂ O ₃)	.627	16.8	3.73	...
Scrap Pyrex glass	.104	44.0	2.6	...
Boron plastic, Monsanto	.081	3.8	2.14	0.078 H ₂
Boron plastic, ORNL (to be reported)	1.07	67	1.6	.027 H ₂

COBALT

Cobalt is estimated to exist in the earth's crust to the extent of 0.001 percent. This can be compared to an estimated nickel content of 0.02 percent.

Africa is by far the largest present source of cobalt, the leading producer being the Belgian Congo which extracts cobalt from the copper-cobalt ores of Katanga province. The extraction of small but consistent amounts of cobalt from copper ores at Mkana, Northern Rhodesia, makes that country the second largest source. French Morocco is the third largest source; in its ore, cobalt is the major metal. Cobalt is presently in great demand for high-temperature alloys and is in extremely short supply. This should be considered seriously by potential users of cobalt in nuclear engineering. The situation will improve somewhat when marginal ores in the United States and Canada are utilized more fully, but the supply will still be less than the demand. The world production of cobalt in 1951 was about 5000 tons/yr, of which about three quarters was produced as the metal.

The June 1952 price of cobalt (rondels containing 97.5 percent cobalt) was \$2.40/lb in 500-lb lots. Electrolytic cobalt of 99.8 percent purity and greater is more expensive, about \$5 to \$10/lb.

HAFNIUM

The earth's crust is estimated to contain 0.0004 percent hafnium which is therefore as plentiful as arsenic, beryllium, germanium, or uranium and more plentiful than mercury, tantalum, niobium, or silver. Hafnium is associated invariably with zirconium minerals, and with the exception of the very rare mineral, thortveitite, the zirconium content of the ore is always appreciably higher than the hafnium content. The richest known sources of hafnium are reported to contain about 35 percent HfO_2 . At present, hafnium is produced entirely as a by-product of zirconium purification, the initial ores being low in hafnium content (about 0.5 to 2.0 percent).

In early 1952, by-product hafnium was being produced in oxide form at the rate of 285 lb of hafnium per month, and 200 lb of sponge hafnium was being made per month. Up to May 1951, 1250 lb of hafnium as the oxide had been produced, and prior to November 1951, Westinghouse Atomic Power Division had produced 550 lb of crystal-bar iodide hafnium.

MERCURY

The earth's crust is estimated to contain less than 0.002 per cent mercury, the only commercial ore at present being cinnabar which contains HgS . Italy and Spain are the principal producers of mercury; their ores average around 5 percent mercury. American deposits which contain less than 0.5 percent mercury, cannot be worked economically under normal conditions, although there was considerable domestic production during the war.

World production in 1950 was estimated to be 136,000 flasks (1 flask = 76 lb) or 10.3 million pounds; of this, the United States produced 4,535 flasks. The price of mercury in April 1952 on the open market was \$210/flask.

RHODIUM

The earth's crust is estimated to contain 0.003 percent rhodium, but this value is not well established. Rhodium is one of the platinum metals and in nature is generally associated with the others in this group. It is less abundant than platinum, palladium, and iridium and more abundant than osmium and ruthenium.

The copper-nickel ores of the Sudbury district of Canada are the largest present source of the platinum metals. Another large source is the deposits of native metal in the Ural Mountains.

SILVER

Silver is estimated to exist to the extent of about 0.0002 percent of the earth's crust. It occurs native and in combination with other elements in a wide variety of minerals. Some ores, especially in Mexico, are mined primarily for their silver content; however, the greater part of the world's supply is produced as a by-product in the treatment of lead, copper, zinc, and gold ores. World production in 1949 was 34,638,896 troy ounces of fine silver. The May 1952 price of silver was \$0.88/troy ounce.

EXTRACTION AND PURIFICATION

BORON

The rasorite deposits of California are nearly pure borax needing only leaching with water and recrystallizing to give commercial borax. This is the largest present source of boron-containing material.

Amorphous boron, in the form of brown powder, can be prepared by reduction of the oxide or halides with magnesium, calcium, or the alkali metals, by electrolysis of fused B_2O_3 , or by thermal decomposition of BN.

The crystalline form can be produced by fusion of the amorphous form in a hydrogen atmosphere or by deposition from the halide on a hot wire. The isotope B^{10} can be most readily separated in large lots by the fractional distillation of $BF_3(CH_3)_2O$ at reduced temperature.

CADMIUM

When zinc ores containing cadmium are distilled, the first distillate is enriched in cadmium. This metal may be separated and then treated for cadmium, either by redistillation or by solution in acid and precipitation with zinc. The cadmium then can be refined electrolytically.

When the electrolyte in zinc-refining operations is purified just prior to electrolysis, the cadmium is precipitated by zinc dust along with other impurities. This precipitate is roasted, redissolved in sulfuric acid, and the cadmium reprecipitated either by zinc dust or electrolytically. The moderately pure cadmium thus obtained is then refined electrolytically in a sulfate bath.

COBALT

The extraction of cobalt from its ores involves a diversity of metallurgical processes, depending on the nature of the ore. Oxide ores from Belgian Congo, for example, are reduced in an electric furnace with lump lime and coke. Moroccan ores are smelted in a blast furnace with coke and limestone to give a speiss. The sulfide ores of Northern Rhodesia are reduced to a matte in a reverberatory furnace. Copper is recovered in a copper converter. The resultant slag, containing the cobalt, is granulated and reduced in an electric furnace. Canadian ores are reduced in a blast furnace. All of these methods give cobalt as the oxide.

The most common method of producing metal from the oxide is by reduction with carbon. The oxide is mixed with 10 percent wood charcoal and an organic binder and pressed into pellets. The pellets are placed in graphite powder in a crucible and heated to $1650^\circ F$ for the required time. The pellets, called "rondels," are cooled in a reducing atmosphere, separated magnetically from the adhering graphite powder, and polished in a tumbling barrel.

Hydrogen reduction is preferred for powders for powder-metallurgy use. Reduction starts below $930^\circ F$ and is rapid at 1290° to $2010^\circ F$.

Electrolytic processes are in some use and probably will replace the carbon-reduction process to a great extent, because refining can be done in the same step. Electrolysis of chloride or sulfate solutions reached considerable importance in Germany during the war. High-purity metal, 99.8 to 99.9 percent pure, was made by dissolving cobalt carbonate in formic acid and electrolyzing.

HAFNIUM

Hafnium is very similar chemically to zirconium and is obtained as a by-product of the production of zirconium. The hafnium compound obtained from the zirconium purification is converted to oxide, chlorinated and the chloride purified and reduced to sponge metal with magnesium. This is strictly analogous to the production of spongy zirconium. To date, the sponge has been used mainly as a feed material for the production of crystal-bar metal by the iodide process. Crystal-bar production likewise is similar to that of zirconium except that a higher iodide decomposition temperature of $2820^\circ F$ is used.

Hafnium also has been produced by calcium reduction of the tetrafluoride in a CaF_2 -lined steel bomb.

MERCURY

Mined and crushed ore is roasted in air yielding SO_2 and metallic mercury vapor which is condensed and the bulk recovered as liquid mercury. This is strained through chamois and bottled in wrought-iron flasks holding 76 lb of mercury. The mercury trapped in the "soot" is recovered by pressing and heating with lime. If purer mercury is desired, it is redistilled and treated with dilute HNO_3 , KOH , and KMnO_4 solutions.

RHODIUM

The material to be treated varies from crude concentrates from the alluvial deposits, containing 73 to 86 percent metal, to secondary slimes, containing as little as 2 percent. The latter materials, containing only small amounts of the platinum metals, ordinarily are concentrated by acid treatment followed by smelting with litharge fluxes and charcoal. This collects the precious metals in the lead and slags off silica and the base metals. Cupellation then yields an alloy containing at least 50 percent platinum-group metals.

The ore concentrates, or the alloys from the slimes, are digested with aqua regia. The solution contains the bulk of the platinum and palladium as well as the gold and most of the base metals present. It also contains small amounts of iridium, rhodium, and ruthenium, which are removed by a series of precipitations and combined with the residue. The bulk of the rhodium, iridium, osmium, and ruthenium remains in the residue.

The residue from the aqua regia treatments is taken into solution by fusion with sodium hydroxide and sodium peroxide, and iridium and rhodium are precipitated. Rhodium is purified, if necessary, by repeating the fusion and precipitation steps.

SILVER

Ore mined primarily for its silver usually is treated by cyanidation, either directly or after concentration. Amalgamation and chloridizing processes also are used to some extent, but they are less efficient.

Gold and silver are precipitated from the cyanide solution with zinc, aluminum, or charcoal and melted down to a bullion.

The anode slimes from lead or copper refining are roasted and then smelted in a reverberatory furnace. This process also yields a silver-gold bullion called "doré metal." Cupellation in the fire refining of lead also yields a similar product.

The bullion is parted by one of the following means:

1. The electrolytic method is preferred if the bullion carries more than 90 percent silver. The doré metal is made anodic in a silver nitrate bath. Pure silver deposits at the cathode, and gold and the platinum metals remain as an anode slime. This slime can be smelted and the gold electrolytically refined from the platinum metal.
2. Dissolving silver out with H_2SO_4 , then precipitating silver with zinc.
3. When gold predominates, the bullion is melted and chlorine is blown through the melt. Silver and the base metals form chlorides which volatilize and leave the gold behind.

PHYSICAL AND CHEMICAL CONSTANTS

The principal physical and chemical constants of the various high-cross-section materials considered here are listed in Tables 1.25.2 through 1.25.11.

**Table 1.25.2—Thermal-neutron-absorption
Cross Section of High-cross-section Materials**

Material	Thermal-neutron-absorption cross section, barns/atom
Boron	750 ± 10
Boron ¹⁰	3990
Cadmium	2400 ± 200
Cobalt	34.8 ± 2
Hafnium	115 ± 15
Mercury	380 ± 20
Rhodium	150 ± 7
Silver	60 ± 3

Table 1.25.3—Densities of High-cross-section Materials

Material	Density,* gm/cm ³
Boron,†	
Calculated	2.33
Crystalline, measured	2.33
Amorphous, measured	2.3
B ₄ C, measured	2.5
BN, measured	2.26
B ₂ O ₃ , measured	1.85
Cadmium, 20°C	
Calculated	8.648
As cast	8.648
As cast, measured at 750°C	7.51
Cold worked	8.694
Volume change on solidification	-4.74%
Cobalt, 20°C	
Calculated	8.836
As cast	8.76
Annealed	8.81
Swaged	8.93
Hafnium	
Calculated	13.36
Measured (crystal bar)	<13.36
Mercury, measured	
0°C	13.595
100°C	13.352
300°C	12.881
Rhodium, 20°C, calculated and measured	12.414
Silver	
20°C, calculated and measured	10.491
700°C, measured	9.89

*Gm/cm³ × 62.43 = lb/cu ft

†See also Table 1.25.1

Table 1.25.4—Melting and Boiling Points of High-cross-section Materials

Material	Melting point, °C	Boiling point, °C
Boron	2000 – 2300	2550
B ₄ C	2350 – 2500	>3500
BN	Sublimes	
B ₂ O ₃	580	
Cadmium	321	765
Cobalt	1495	2900
Hafnium	2130 ± 15	?
Mercury	-38.87 ± 0.02	356.9
Rhodium	1966 ± 3	4500
Silver		2212
In vacuum or under charcoal	960.5	
In equilibrium with oxygen of air of atmospheric pressure	950	

Table 1.25.5—Heats of Fusion and Heats of Vaporization of High-cross-section Materials

Material	Heat of fusion, cal/mole	Heat of vaporization (25°C), cal/mole
Boron	...	90,000
Cadmium	1460	26,750
Cobalt	3660	105,000
Hafnium
Mercury	560	14,690
Rhodium	5200	138,000
Silver	2855	70,000

Table 1.25.6—Heat Capacities of High-cross-section Materials

Material	Heat capacity,*† Cp, cal/(mole)(°C)	Temp. range, °C
Boron	$1.54 + 4.40 \times 10^{-3}T$	25 – 927
B ₄ C	$22.99 + 5.4 \times 10^{-3}T$	25 – 1427
BN	$1.82 - 3.62 \times 10^{-3}T$	25 – 927
B ₂ O ₃	$8.73 + 25.40 \times 10^{-3}T - 1.31 \times 10^{-5}T^2$	25 – 450
Cadmium	$5.31 + 2.94 \times 10^{-3}T$	25 – 321
	7.10	321 – 827
Cobalt		
α	$4.72 + 4.30 \times 10^{-3}T$	25 – 4450
β	$3.30 + 5.86 \times 10^{-3}T$	445 – 1127
γ	9.60	1127 – 1490
Hafnium	$6.00 + 0.524 \times 10^{-3}T$	25 – 2227
Mercury, under 1 atm		
	6.697	0
	6.575	100
	6.505	200
	6.509	400
Rhodium	$5.49 + 2.06 \times 10^{-3}T$	25 – 1627
Silver	$5.09 + 2.04 \times 10^{-3}T + 0.3610^{-5}T^2$	25 – 961

*Cal/(mole)(°C) × 1 = Btu/(lb mole)(°F)

†T in °K

Table 1.25.7—Enthalpy of High-cross-section Materials

Material	Enthalpy ($H_{T^{\circ}\text{C}} - H_{25^{\circ}\text{C}}$), cal/mole				
	127°C	327°C	527°C	727°C	1127°C
Boron	300	1,080	2,040	3,130	
B ₄ C	1,640	5,780	8,180	16,380	27,620
BN	315	1,035	1,450	2,420	
B ₂ O ₃	1,640	1,640	8,350	19,860	35,110
Cadmium	645	3,450	4,870	6,290	
Cobalt	640	2,010	3,550	5,250	9,520(γ)
Rhodium	630	1,920	3,300	4,290	8,010
Silver	615	1,885	3,195	4,505	10,380
Hafnium	645	1,895	3,170	4,465	7,110
Mercury	100°C	200°C	300°C	400°C	500°C
($H_{T^{\circ}\text{C}} - H_{-38.83}$)	924.5	1578.5	2228.1	2878.2	3533.5

Table 1.25.8—Entropy of High-cross-section Materials

Material	$S_{25^{\circ}\text{C}}$	Entropy, ($S_{T^{\circ}\text{C}} - S_{25^{\circ}\text{C}}$), cal/(mole)(°C)				
		127°C	327°C	527°C	727°C	1127°C
Boron	1.7 ± 0.2	0.87	2.43	3.80	5.01	...
B ₄ C	6.47 ± 0.03	4.69	13.01	20.10	26.15	35.78
BN		0.91	2.36	3.63	4.78	...
B ₂ O ₃	13.04 ± 0.07	4.71	13.23	28.61	35.41	45.67
Cadmium	12.34 ± 0.10	1.86	7.04	9.08	10.67	...
Cobalt	6.86 ± 0.10	1.84	4.61	6.81	8.71	12.26(γ)
Rhodium	7.6 ± 0.5	1.81	4.42	6.40	8.06	10.76
Silver	10.20 ± 0.05	1.78	4.35	6.23	7.78	12.56
Hafnium	13.1 ± 0.2					
Mercury (absolute entropy of liquid)		100°C 19,607	200°C 21,159	300°C 22,405	400°C 21,449	500°C 24,353

Table 1.25.9—Resistivities of High-cross-section Materials

Material	Resistivity, ohm-cm			
	0°C	100°C	300°C	600°C
Boron, pressed powder	1.8×10^6	13,200	36(320°C)	0.08
Cadmium	7.54(18°C)	9.82	16.50	
Cobalt	5.6	9.5	18	39
Hafnium	32.7	47.1	75.0	106.3
Mercury	94.07	103.25	127.00	
Rhodium	4.3	6.2	10.4(309°C)	14.9(511°C)
Silver	1.47	2.07	3.33	6.80(800°C)

Table 1.25.10—Coefficients of Linear Thermal Expansion of High-cross-section Materials

Material	Linear coefficient of thermal expansion, per °C	Temp. Range, °C
Boron, crystalline	8.3×10^{-6}	20 – 750
B ₄ C, molded	4.5×10^{-6}	25 – 800
Cadmium	31.8×10^{-6}	20 – 100
Cobalt	14.2×10^{-6}	30 – 200
	15.0×10^{-6}	200 – 400
	24.0×10^{-6}	400 – 500
Hafnium	5.9×10^{-6}	0 – 1000
Rhodium	12.1×10^{-6}	0 – 1500
Silver	20.61×10^{-6}	0 – 500
Silver-Cadmium alloys		
80% Ag – 20% Cd	22.0×10^{-6}	0 – 538
75% Ag – 25% Cd	22.9×10^{-6}	0 – 538
70% Ag – 30% Cd	24.0×10^{-6}	0 – 538
Mercury, cubic coefficient		
$V_t = V_0(1 + 0.18182 \times 10^{-3}t + 0.00078 \times 10^{-6}t^2)$ where $t = ^\circ\text{C}$		

Table 1.25.11—Thermal Conductivities of High-cross-section Materials

Material	Thermal conductivity,* cal/(sec)(cm)(°C)	
B ₄ C		
100°C	0.29†	0.16‡
300°C	.22†	.14‡
500°C	.18†	.115‡
700°C	.155†	.095‡
Cadmium		
Room temperature		0.22
435°C		.114
Cobalt		
30°C		0.165
Mercury		
0° – 100°C		0.020
Rhodium		
0°C		0.213
17°C		.210
100°C		.191
Silver		
0°C		0.999
100°C		.934
300°C		.864
400°C		.844
500°C		.876
Silver-cadmium alloys (100° – 400°C)		
5.4 wt-% Cd		0.61
12.9 wt-% Cd		.46
22.0 wt-% Cd		.38
24.5 wt-% Cd		.37
31.8 wt-% Cd		.35
35.7 wt-% Cd		.33

*Cal/(sec)(cm)(°C) $\times (2.419 \times 10^2)$ = Btu/(hr)(ft)(°F)†Density = 2.5 gm/cm³‡Density = 1.9 gm/cm³

ALLOTROPY**BORON**

Two crystal forms of boron seem to coexist, one tetragonal and the other hexagonal.

CADMIUM

No allotropic modifications of cadmium have been confirmed.

COBALT

There is a well-established transformation from the hexagonal close packed to the face-centered cubic structure at 420°C. Heat of transformation is 5.9 cal/mole. The reverse transformation has been reported at 800° to 1000°C, but this has not been confirmed.

HAFNIUM

There is a transformation from hexagonal close packed to body-centered cubic at 1950° ± 100°C.

MERCURY

No allotropy is known to exist.

RHODIUM

A second face-centered cubic modification is said to exist and be stable up to 1000°C. The two phases are said to coexist at room temperature.

SILVER

No allotropy is known to exist.

CRYSTALLOGRAPHY**BORON**

Material	Crystal form	a_0 , Å	c_0 , Å	α
Boron	Tetragonal	8.57	8.13	...
Boron	Hexagonal	11.98	9.54	...
B ₄ C	Rhombohedral	5.19	...	66°18'
BN	Hexagonal	2.51	6.69	...
B ₂ O ₃	Cubic	10.035

CADMIUM

Cadmium has a close-packed hexagonal lattice with

$$a_0 = 2.9787 \text{ Å}$$

$$c_0 = 5.6173 \text{ Å}$$

Slip plane is (0001), slip direction, $[11\bar{2}0]$. Twinning plane is $(10\bar{1}2)$.

COBALT

Form	Stability range, °C	Crystal structure	Room temperature constants, Å	
			a_0	c_0
Alpha	To 440	hcp	2.5071	4.0693
Beta	Above 440	fcc	3.5439	...
Gamma*	Above 800*	hcp*

*Unconfirmed

HAFNIUM

Below approximately 1660°C, hafnium has a hexagonal close-packed structure with $a_0 = 3.1883$ Å, $c_0 = 5.0422$ Å. Above approximately 1950°C, it has a body-centered cubic structure. Preferred orientation after rolling is the same as described for zirconium in Chap. 1.24.

MERCURY

Solid mercury at -46°C is rhombohedral with $a_0 = 2.999$ Å and $\alpha = 70^\circ 32'$. It corresponds to a close-packed cubic structure deformed by compression along a cube diagonal.

RHODIUM

Rhodium has a face-centered cubic lattice with $a_0 = 3.8037$ Å at 20°C. A second structure, complex cubic, is said to coexist with the above at room temperature and may be the only stable phase at extremely low temperatures. It is not stable above 1000°C. Lattice dimension a_0 , for this second structure is 9.2205 Å. Confirmation is lacking for the complex structure.

SILVER

Silver has a face-centered cubic lattice with $a_0 = 4.0860$ at 18°C.

HEALTH HAZARDS**CADMIUM**

The salts of cadmium as well as the metal and oxide vapors are poisonous. Inhalation or ingestion should be avoided. Competent industrial medical authorities should be consulted regarding handling of this material.

MERCURY

Mercury is poisonous, so that precautions against inhalation or ingestion should be taken. Good housekeeping is of prime importance. Specific instructions are available from industrial medical personnel.

HANDLING AND STORAGE**HAFNIUM**

The oxide formed on hafnium is somewhat more protective than that formed on zirconium. Therefore, it is handled more readily in air.

MERCURY

Mercury for most uses can be handled and stored in iron containers. For behavior of mercury with specific material see: *Liquid Metals Handbook*, NAVEXOS P-733, June 1, 1950.

MECHANICAL PROPERTIES

The mechanical properties of boron, cadmium, cobalt, hafnium, rhodium, and silver are listed in Tables 1.25.12 through 1.25.18, respectively.

Table 1.25.12—Mechanical Properties of Boron and Boron-containing Materials

Tensile strength, lb/sq in.	
Massive B_4C	10,000
"Boral" (50% B_4C in aluminum matrix)	5,500
Boron steel, containing 1.6 – 1.8% boron, after annealing at 1350°F	73,000
Compressive strength, lb/sq in.	
Boron bonded with B_2O_3 ,	
95% total boron	>50,000
99% total boron	>36,000
Boron bonded with 37% lead borate	50,000
Boron bonded with 10% lucite or polystyrene	<20,000
Hardness, Mohs scale	
Diamond	10.0
B_4C	9.32
Boron	9.3
BN	1.2
Impact	The impact resistance of boron and boron carbide shapes is poor
Creep	Boron carbide does not creep, work, or "season" under stress at room temperature; elevated temperature data are unavailable

Table 1.25.13 — Mechanical Properties of Cadmium

Tensile properties	Ultimate strength, lb/sq in.	Elongation, %
As cast, 68°F	2,500 – 9,000	
Sheet		
–4°F	18,800	9.5
–103°F	30,600	5
99.95% cadmium chill cast and aged at room temperature	10,300	50
99.95% cadmium cold worked 70%, aged at room temperature	13,700	126
Modulus of elasticity, 10 ⁶ lb/sq in.		7.1 to 10.0
Shear modulus, 10 ⁶ lb/sq in.		1.4 to 3.6*
Poisson's ratio		0.30
Hardness, Brinell Number of chill cast to 1-in. diameter		21-23

*This range is reported in NBS Circular 447

Table 1.25.14 — Mechanical Properties of Cobalt

Ultimate strength,* lb/sq in.	34,400
Compressive strength,* lb/sq in.	122,000
Modulus of elasticity, 10 ⁶ lb/sq in.	30.0
Shear modulus, 10 ⁶ lb/sq in.	11.1
Hardness, Brinell Number	
68°F	174
280°F	222

*Cast 99.73% cobalt

Table 1.25.15— Mechanical Properties of Hafnium

Tensile properties*†						
Material	Test temperature, °F	Yield strength (0.2% offset), lb/sq in.	Yield strength (0.5% offset), lb/sq in.	Ultimate tensile strength, lb/sq in.	Total elongation in 3 in., %	Reduction of area, %
WAPD	75	34,950	41,550	64,600	43	30
WAPD	650	26,000	29,100	41,000	58	36
Foote	75	44,000	50,000	72,700	39	28
Foote	650	31,800	35,000	46,100	55	35
Modulus of elasticity, 72°F, 10 ⁶ lb/sq in.					14.0	
Creep, 650°F						
		Stress, lb/sq in.	Minimum creep rate,‡ in./in./hr			
		35,500	1.9 × 10 ⁻⁶ to 2.0 × 10 ⁻³			
		29,500	7.0 × 10 ⁻⁷ to 1.8 × 10 ⁻⁵			
Notched-bar impact (V-notch Charpy specimen), ft-lb, Specimen cut in longitudinal direction and notched in the transverse direction						
		Notched-bar impact strength				
Test temperature, °F		Foote	WAPD			
-328		5.0	4.5			
-112		5.5	7.5			
32		8.5	22.0			
217		15.0	26.0			
390		22.0	38.5			
572		52.5	54.5			
Welded material: notch in the weld metal						
		Notched-bar impact strength				
Test temperature, °F		Foote	WAPD			
-328		3.0	3.5			
-112		5.0	5.0			
32		11.0	7.0			
212		16.0	9.0			
443		32.0	24.0			
563		28.0	45.0			

*Arc-melted crystal bar; hot rolled 1700°F; cold rolled 5%, annealed 1 hr in vacuum, 1470°F; 3-in. gauge length, 1 × 0.04-in. section

†The spread in tensile properties of the two grades, reflects the purity of the metal. Hafnium is strengthened by relatively small amounts of oxygen, nitrogen, or carbon

‡The wide range indicates considerable variation in the material tested

Table 1.25.16 — Mechanical Properties of Rhodium

Tensile strength, 10^3 lb/sq in.	
Annealed	73
Hard drawn	300
Modulus of elasticity, 10^6 lb/sq in.	
Hard-drawn wire	42
Hardness, Brinell Number	
Cast	140
Cold rolled	260
Annealed	55-155
Annealed, 2190°F	122
Wear	The resistance of electrodeposited rhodium to wear is exceptional, even under heavy pressure

Table 1.25.17—Room-temperature Mechanical Properties of Silver

Material	Condition	Young's modulus, 10 ⁶ lb/sq in.	Proportional limit, lb/sq in.	Yield point, lb/sq in.	Ultimate tensile strength, lb/sq in.	Elongation in 2 in., %	Reduction of area, %	Hardness	Modulus of shear 10 ⁶ lb/sq in.	Poisson's ratio
Ag, 1000 fine	Rod, 0.8 in. diam., rolled, annealed 10 min, 930°F	10.3	700	1,506	21,500	65	92
Ag, 999 fine	Sheet, 0.032 in. 50% cold-reduc- tion	44,300	54,300	2.4	...	R _f 91
Ag, 999 fine	Sheet, 0.032 in., 50% cold-reduc- tion, annealed ½ hr, 1400°F	7,800	22,500	48	...	R _f 98
Ag, commercial purity	Hard drawn	10.9	3.9	0.392
Ag, commercial purity	Annealed	10.6	0.369
Ag, commercial purity	Chill cast	...	2,000	4,700	15,400	80	67
Ag, commercial purity	Sand cast	...	1,000	3,400	15,300	41	38

Table 1.25.18 — Mechanical Properties of Ag-Cd Alloys

Alloy	Temp., °F	Ultimate tensile strength, lb/sq in.	Yield strength (0.2% offset), lb/sq in.	Elongation in 3 in., %	Young's modulus, 10 ⁶ lb/sq in.
80 Ag, 20 Cd	70	29,500	5,300	76	10.5
	400	9.7
	600	15,500	6,350	15	9.2
75 Ag, 25 Cd	70	12.7
	400	11.7
	600	15,500	6,400	...	11.1
70 Ag, 30 Cd	70	11.3
	400	10.4
	600	16,200	9.8
62 Ag, 38 Cd	600	...	7,500
67 Ag, 30 Cd, 3 Cu*	600	...	13,500

*Copper in small amounts hardens the silver-cadmium alloys. Nickel and aluminum perform the same function

MELTING AND CASTING

BORON

Boron can be melted in a B₄C crucible and, under nitrogen pressure, in a BN crucible. Molten boron carbide dissolves considerable excess carbon which separates out as plates of graphite on cooling.

"Boral" is prepared by mixing B₄C(50 percent) powder with half the necessary aluminum and adding the mixture to the remaining aluminum in the molten condition. The temperature is critical. The material is cast into steel molds from 1230° ± 20°F.

Boron steels containing 1 to 2 percent boron are made in electric furnaces using an ingot-iron charge. Iron ore is added after melt down and before the boron addition to minimize the manganese which must be kept low because of radiation considerations. Carbon is also low in these steels. These boron steels have been cast in 10-in.-square, big-end-up ingot molds. The conventional boron-treated steels of industry contain much less boron than this; 0.001 to 0.006 percent maximum.

CADMIUM

Melting and casting cadmium offer no particular problems. Mild-steel or cast-iron crucibles may be used; cadmium can be die cast.

COBALT

Cobalt is melted satisfactorily in magnesia and beryllia crucibles. A protective atmosphere is preferred to prevent pickup of oxygen and nitrogen. Pouring temperatures of about 2900°F are satisfactory, and deoxidation is necessary. When rondels are melted, boiling occurs as a result of completion of the oxide-reduction process. Molds satisfactory for steel generally are satisfactory for cobalt.

HAFNIUM

Arc melting in an inert atmosphere in water-cooled copper crucibles is the currently preferred method of melting hafnium. The technique is very similar to that for melting zirconium. Casting is not practiced with this technique.

MERCURY

Mercury is liquid at room temperature. It can be cast by pouring into molds chilled below the freezing point.

RHODIUM

Induction melting is preferred for rhodium. Zirconia or thoria crucibles are best, and an oxidizing atmosphere is desirable during the initial melting stages. A preliminary solidification followed by remelting is desirable to eliminate gases. Slight reduction with CO may be advisable just before pouring, or minute amounts of deoxidizers such as calcium boride can be added. However, if the metal is poured at a temperature only slightly above the liquidus, gas difficulties are minimized. Oxyhydrogen-flame melting in a lime crucible is also practiced.

Heated graphite molds generally are used, but nickel molds that have been oxidized and coated with zirconia or copper molds coated with zirconia sometimes are used. Care must be taken to avoid cold shuts when metal molds are used.

SILVER

The biggest problem involved in the melting and casting is the high solubility of oxygen in molten silver which is later evolved on solidification. To avoid porosity in silver castings, it is necessary to minimize contact of the silver with oxygen and air or to use a deoxidation practice. Melting under a layer of charcoal gives adequate protection,

FORMING AND FABRICATION

BORON

Boron and boron carbide shapes can best be formed by powder-metallurgy techniques. B_2O_3 makes a satisfactory binder although it is hygroscopic; 10 to 30 weight-percent is used. Lead borate results in a more satisfactory bond and avoids moisture pickup. With both bonding materials, the mixed powders are hot pressed in graphite dies at 1470° to 1830°F.

Boron or boron carbide can be compacted with 10 percent lucite binder in a steel die at 250°F. If polystyrene is used instead of lucite, a temperature of 300°F is necessary.

Boron carbide is self sintering if pressed in graphite at 4000°F. The Norton Co. produces commercial shapes by this method. Boron carbide compacts have been made with metal bonds usually by powder-metallurgy methods. Aluminum is unsatisfactory as a binder above 1110°F. Nickel-bonded compacts alloy and form a low-melting eutectic at 2000°F. For this reason, copper and iron are better bonding materials above 1830°F. These metal-bonded materials are pressed and sintered to the desired shape.

"Boral" ingots, prepared as indicated under melting and casting, are fabricated by the following process. The somewhat porous ingot is sprayed with aluminum to cover any exposed B_4C . The ingot is wrapped with $\frac{1}{8}$ -in. 2S aluminum sheet and rolled at 1130°F with 10 percent reduction per pass. Heat is developed from deformation during rolling, so that reheating is unnecessary. The finished $\frac{1}{4}$ -in. sheet has 0.020 in. of 2S aluminum on each surface and can be further rolled or hot pressed to desired shape.

Low-density (1.8 gm/cm^3), boron carbide bricks, which are brittle and have poor impact strength but which are strong enough to cement to wood or metal backings, are prepared at a much lower cost than commercial, self-sintered B_4C bricks. Commercial minus-325-mesh powder is mixed with water to make a thick mud, then compression molded to shape with 8000 lb/sq in. pressure. The bricks are baked at 1110° to 1830°F . They are stronger when baked at 1830°F but are more hygroscopic than when baked at lower temperatures. They completely deteriorate in water.

Boron coatings can be produced by high-temperature evaporation of metallic boron at 4530°F and a pressure of 5 to 10 mm of mercury. The bright surface is superior to platinum in reflecting power. Boron is also available in flame spraying mixtures to produce coatings.

Thermal decomposition of diborane (B_2H_6) at 660° to 840°F and 1.5 to 2.0 mm mercury pressure deposits suitable boron coatings on a number of surfaces.

Boron can be "cemented" or "diffused" into ferrous materials from boron or ferroboration powder by a 1- to 5-hr treatment at 1290° to 2010°F . The rate of cementation increases rapidly at the A_3 temperature. Nickel and nickel-chromium steels are more rapidly "cemented" with boron than mild steels.

Ferroboration is produced by electric-furnace reduction of ores such as rasorite or colemanite in the presence of iron-containing ores.

Boron nitride can be produced by a variety of methods.

The 1.55 to 1.75-percent-boron steels are forged at 1875° to 1900°F , and finished at 1425°F . There is a tendency to edge-crack during rolling. Balls, $\frac{5}{16}$ in. in diameter, are made from this material by hot forging or cold heading.

A 2 percent-boron steel is forged or rolled to 2×2 -in. section, then further rolled to 1-in.-diameter round without difficulty.

Cold extrusion of some of the boron, boron nitride, or boron carbide mixes with binders may be feasible. This would be followed by a sintering operation.

CADMIUM

Forging or rolling cadmium increases the hardness temporarily. Maximum hardness is reached one day after the operation but is followed by rapid softening in the interval from 10 to 100 days. The subsequent aged product may be softer than the as-cast structure.

Cold rolling temporarily increases the tensile strength, but recrystallization occurs slowly at room temperature.

Cadmium may be extruded or drawn into wire with no particular difficulty.

COBALT

Cobalt has been extruded with a 4:1 reduction ratio. Extrusion temperatures of 1290°F gave better surface than 1470°F . Steel cladding prevented surface contamination. Cobalt has been rolled satisfactorily at 1830°F clad in SAE 1020 steel. Cobalt can be swaged at 1110°F , but results at 750° and 1470°F were not satisfactory. Cobalt can be cold worked and can be drawn into fine wire.

HAFNIUM

FORGING

Hafnium forges readily at 1700°F .

HOT ROLLING

Hot rolling of hafnium should begin at 1650° to 1700°F , and finishing temperatures should not be any lower than 1380°F if recrystallization is desired.

COLD ROLLING

When cold rolling hafnium, cold work should be confined to less than 35 percent, and short intermediate anneals at 1470°F should be used. Cracking is serious at 50 percent cold reduction.

EXTRUSION

Extrusion of hafnium should be feasible.

DRAWING

The oxide from a 1470°F anneal plus a chlorinated oil provides satisfactory lubrication for cold drawing. Reductions should be kept to 35 percent or less and followed by intermediate 1470°F anneals as necessary.

RHODIUM

FORGING AND ROLLING

Rhodium is best worked from small ingots, not more than $\frac{1}{2}$ to $\frac{3}{4}$ in. thick. Rhodium requires an initial hot reduction at about 2010°F, but after it has been worked down to about 0.1 in., it can be cold rolled. Annealing is required after each 30- to 40-percent reduction. Annealing at high temperatures should be avoided because recrystallized metal of the usual purity is brittle. Suitable annealing temperatures are 1380° to 1470°F, but for high-purity metal, annealing should be preceded by a 10- to 20-percent-HCl pickle to remove iron or other base metal.

DRAWING

At the start, wire is drawn at 2010°F, but the temperature is allowed to decrease as the reduction increases (to about 1290°F for 0.020-in. wire). Further reduction is carried out cold with anneals at 1380° to 1470°F following each 50 to 75 percent reduction. Anneals at higher temperatures should be avoided because of brittleness resulting from recrystallization. Palm oil, soap powder, or one of the softer wire-drawing soaps may be used as lubricants for drawing on the block. For finer wire drawn on continuous multiple-die machines, emulsions of oil, soap, and water are employed; for extremely fine wire, natural fish oils may be effective.

ELECTRODEPOSITION

In many applications, a thin film of rhodium formed by electrodeposition is desired. Rhodium can be deposited directly on precious metals. On ferrous metals, tin, lead, zinc, cadmium, and aluminum, an undercoat of nickel (or preferably silver) is necessary for best results. Using a highly polished undercoat of silver, no polishing is required after the deposition of rhodium. The heaviest practical deposit is 0.002 in.; for protection against tarnish, 0.000015 to 0.00002 in. is generally sufficient.

SILVER

Conventional hot- or cold-forming methods are suitable for silver. Silver coatings may be applied by welding, spraying, cladding, hot-dipping, electroplating, chemical-reduction, vaporization, or cathode-sputtering techniques. Of these, cladding and electroplating are the most common.

POWDER METALLURGY

COBALT

Hydrogen-reduced cobalt is preferred for powder-metallurgical uses. Cobalt is used as a binder for cemented carbide materials. In this application, however, the compacts are heated above the melting point of the cobalt powder they contain.

RHODIUM

Powder-metallurgy compacts can be worked as described under the fabrication section. More frequent anneals are necessary, however.

SILVER

Powder-metallurgy techniques have been used for silver and especially for silver alloys, such as Ni-Ag, which are impossible to produce by conventional methods.

JOINING

BORON

The 1.55- to 1.75-percent-boron steels have been welded satisfactorily by an electric arc or a torch. The "Boral" alloy is difficult to weld. The boron and boron carbide sintered materials are not amenable to joining operations.

HAFNIUM

Brazing and soldering methods for hafnium have not been developed. Welding is best done in an inert atmosphere (helium or argon) using a tungsten electrode and fillet metal. Large or complicated structures should be given a 1470°F strain anneal in a jig after welding. This will minimize distortion on subsequent machining.

SILVER

Silver, as such, or as a constituent of lower melting alloys, has been used as a brazing or soldering material. Silver may be fusion-welded; it may also be pressure-welded at slightly elevated temperatures, even at room temperature if proper precautions of cleanliness are taken.

MACHINING

BORON

Machining of boron and boron carbide sintered materials is limited to cutting with abrasive wheels and grinding; diamond wheels are preferred. In some cases, silicon carbide wheels are satisfactory. The "Boral" alloy can be readily sheared, sawed, punched, drilled, or tapped. The 1.50- to 2.00-percent boron steels can be machined successfully with carbide tools.

CADMIUM

Cadmium machines much like other soft metals.

COBALT

Cobalt can be machined by practices normally employed for mild steel.

HAFNIUM

Hafnium is easier to machine than zirconium. High-speed steel tools are satisfactory.

RHODIUM

Machining does not appear to present any serious problems.

SILVER

With currently available tool grinding techniques, clogging of the cutting tool can be avoided, and silver can be machined satisfactorily.

HEAT TREATMENT**BORON**

Self-sintered boron carbide compacts can be heat treated to eliminate carbon and nitrogen absorption. This is done by heating the part in an atomic hydrogen flame, then cooling in a jet of cold hydrogen. The 1.50- to 2.00-percent boron steels get their full hardenability by heating at 1800° to 1850°F, followed by a water quench.

CADMIUM

Annealing temperature is about 250° to 175°F as the cold reduction varies from 20 to 80 percent. Recrystallization is reported to occur slowly at room temperature.

COBALT

Heat-treating practices should take into account the sluggish nature of the α - β transition.

HAFNIUM

Heat treatment of hafnium consists mainly of annealing to relieve stress and promote recrystallization. The recrystallization range is 1290° to 1470°F.

RHODIUM

The only heat treatment practiced for rhodium has been an annealing operation at 1380° to 1470°F for softening after cold work. An inert atmosphere is preferred. Recrystallization and grain growth take place rapidly at temperatures above 1470°F. Metal of ordinary purity in the recrystallized state is brittle.

SILVER

A temperature of 1650°F is necessary for complete annealing in less than a half hour. Apparently, recrystallization starts at fairly low temperature, but grain growth does not occur appreciably below 1290° to 1470°F. The recrystallization and grain-growth temperatures vary with the amount and types of impurities.

METALLOGRAPHY

HAFNIUM

The metallography of hafnium is similar to that of zirconium. A 45-percent nitric, 5-percent-hydrofluoric acid mixture is a good pickling and etching solution.

RHODIUM

Rhodium is best etched electrolytically using an alternating current in a bath of 20 percent sulfuric acid in water.

SILVER

Flow of metal should be kept to a minimum during polishing because working effects may persist to a considerable depth below the surface. Techniques used for other soft metals probably would work well. An electrolytic etch in 5-percent KCN solution is satisfactory.

CORROSION BEHAVIOR

BORON

Boron oxidizes in air at 210°F. At higher temperatures it burns with a green flame. The oxygen in air inhibits the production of BN, but 99.4 percent nitrogen reacts to produce BN at 1830°F or higher. Boron reacts with NH_3 at 570°F to give BN. Boron ignites in fluorine at room temperature and in the other halogens at higher temperatures.

Boron nitride, BN, is stable in air at room temperature. It will ignite in oxygen when heated. There is no change in hydrogen to a red heat. Boron nitride is oxidized by CO_2 ; but the resulting B_2O_3 protects the BN from further oxidation. Boron nitride reacts with gaseous HCl at 1200° to 1830°F. It is rapidly attacked by HF. Boron nitride is not attacked by boiling water but is completely hydrolyzed by steam.

Boron carbide in the massive form is resistant to air at 1830°F. In this, it is superior to diamond. The oxidation rate is about ten times that of SiC.

Boron or boron carbide compacts bonded with B_2O_3 are unstable in moist air and deteriorate in water. This difficulty does not occur when lead borate is used as a binder.

The 1.50- to 2.00-percent boron steels have no better corrosion resistance than mild steels.

CADMIUM

Moist air oxidizes cadmium superficially, forming a gray-white film which inhibits further corrosion. At 570°F in air, a brown oxide film forms, but further corrosion is inhibited. At higher temperatures, the oxide is volatile and oxidation goes to completion.

The metal does not react with boiling water; cadmium vapor decomposes steam. Cadmium is attacked readily by HCl, H_2SO_4 , and especially HNO_3 . It dissolves slowly in acetic acid. Cadmium combines directly with the halogens in aqueous solution.

COBALT

Cobalt is intermediate between nickel and mild steel in regard to corrosion in air. Oxidation is accelerated by moisture. Finely divided cobalt occludes considerable volumes of hydrogen. Cobalt is not attacked by cold or boiling water. Cobalt is attacked intergranularly by 1830°F lithium. It also is attacked seriously by 1830°F bismuth.

Cobalt dissolves readily in the common mineral acids, but only slowly in hydrofluoric acid. It dissolves with difficulty in ammonium hydroxide and is attacked slowly by sodium hydroxide solutions.

HAFNIUM

ATMOSPHERIC

The oxidation resistance of hafnium is fairly good and somewhat better than that of zirconium. After 2 hr in still air at 1740°F, it shows a penetration of only 0.15 mm.

WATER

Hafnium is superior to zirconium in corrosion resistance to water at 550°, 600°, and 650°F and steam at 750°F and 1500 lb/sq in. Unlike zirconium, it is not sensitive to small amounts of impurities, such as nitrogen.

OTHER

In a 50-percent aqueous solution of NaOH, penetration is at the rate of 0.00018 in./yr.

MERCURY

Air, oxygen, NO, NO₂, and CO₂ at ordinary temperatures have no effect on mercury. Mercury is oxidized in air at 660°F; the oxide decomposes at higher temperatures.

Mercury is insoluble in HCl and slightly soluble in cold dilute HNO₃ or aqua regia. It is attacked rapidly by hot or concentrated HNO₃, by the halogens, and by ozone. It is a reducing agent toward permanganate, dichromate, persulfate, ferric salts, and nitrobenzene.

Liquid Metals Handbook, NAVEXOS P-733, discusses solubilities of the following materials in mercury: tungsten, molybdenum, chromium, beryllium, tantalum, niobium, silicon, titanium, nickel and its alloys, copper and its alloys, cobalt and stellite, platinum, manganese, zirconium, aluminum, bismuth, cadmium, cerium, gold, lead, magnesium, silver, tin, zinc, glass, ceramics, and graphite.

RHODIUM

ATMOSPHERIC

Rhodium is oxidized superficially by air at temperatures above about 1010°F; the oxide dissociates at about 2010°F.

WATER

Rhodium does not corrode in water at any temperature.

OTHER

Rhodium resists corrosion by most common acids including boiling aqua regia. It is attacked somewhat by hydrobromic acid, particularly when hot, by moist iodine, and by sodium hypochlorite. Hot, fuming sulfuric acid also attacks it. It is attacked by chlorine and bromine above 480°F.

SILVER

Exposure to pure, dry or moist air, or dry or moist oxygen, at ordinary temperatures and pressures does not affect silver. Tarnishing of silver in ordinary atmospheres is caused by sulfur compounds, generally hydrogen sulfide.

Moisture accelerates the oxidation of silver. For example, in sealed tubes in dry air or oxygen, silver disintegrated at temperatures above 930°F but not below. In similar experiments in moist air or oxygen, disintegration was not noticeable at 210°F but was appreciable at 390°F.

Silver is not affected by pure water at room temperature or boiling water, nor is it attacked by steam. It has poor corrosion resistance in oxygenated water at 500°F. Resistance of silver to corrosion by a great number of media is discussed by A. Butts and J. M. Thomas in a chapter in *Silver in Industry*.

SILVER-CADMIUM ALLOYS

Silver and an 88-weight-percent silver:12-weight-percent cadmium alloy had poor corrosion resistance in oxygenated 500°F water. An 80-weight-percent silver:20-weight-percent cadmium alloy had fair resistance in nonoxygenated, 500°F water. The following alloys had poor resistance in oxygenated, 600°F water and better, but still not good, resistance in nonoxygenated, 600°F water:

80 weight-percent Cd:20-weight-percent Ag
75 weight-percent Cd:25-weight-percent Ag
70 weight-percent Cd:30-weight-percent Ag

CONSTITUTIONAL DIAGRAMS

BORON

The aluminum-boron and iron-boron systems are discussed in the *1948 ASM Metals Handbook*.

In *Constitution of Alloys Bibliography*, by J. L. Haughton, references to the following systems involving boron are given: aluminum, barium, bismuth, calcium, cerium, chromium, cobalt, copper, gold, iron, lead, nickel, palladium, silver, strontium, thallium, thorium, tin, and tungsten.

CADMIUM

Alloys of cadmium with the following elements are discussed in the *1948 ASM Metals Handbook*: aluminum, antimony, bismuth, iron, lead, magnesium, mercury, nickel, silver, tin, and zinc.

References to systems involving the following additional metals with cadmium are given in *Constitution of Alloys Bibliography*, by J. L. Haughton: arsenic, calcium, carbon, chromium, cobalt, copper, gallium, gold, indium, lithium, palladium, phosphorus, platinum, polonium, potassium, rhodium, selenium, silicon, sodium, strontium, tellurium, and thallium.

COBALT

Constitutional diagrams involving cobalt with the following other metals are discussed in the *1948 ASM Metals Handbook*: aluminum, carbon, copper, iron, nickel, platinum, silver, and tungsten.

Work on diagrams is referred to in *Constitution of Alloys Bibliography*, by J. L. Haughton: antimony, arsenic, beryllium, bismuth, boron, cadmium, cerium, chromium, gold, hydrogen, lead, magnesium, manganese, mercury, molybdenum, niobium, nitrogen, oxygen, palladium, phosphorus, potassium, selenium, silicon, sodium, sulfur, tantalum, tellurium, thallium, tin, titanium, vanadium, zinc, and zirconium.

HAFNIUM

The phase diagram of the zirconium-hafnium system consists of complete solid solubility above and below the α - β transition. Other systems have not been reported.

MERCURY

The 1948 edition of *ASM Metals Handbook* discusses alloys of mercury with the following metals: bismuth, cadmium, iron, silver, tin, and zinc.

Constitution of Alloys Bibliography, by J. L. Haughton, gives references to systems involving mercury with the following elements: aluminum, arsenic, barium, calcium, cerium, chromium, cobalt, copper, gallium, gold, indium, lanthanum, lead, lithium, magnesium, manganese, molybdenum, neodymium, nickel, platinum, potassium, praseodymium, rubidium, selenium, sodium, strontium, tellurium, thallium, thorium, titanium, tungsten, uranium, and vanadium.

RHODIUM

Constitutional diagrams of rhodium and the following metals have been studied and are discussed in the references in the selected bibliography: copper, gold, nickel, palladium, platinum, and silver.

References to work involving rhodium with the following additional metals are given in J. L. Haughton's *Constitution of Alloys Bibliography*: bismuth, iron, phosphorus, scandium, tellurium and zinc.

SILVER

Phase relations of silver with the following elements are discussed in *Silver in Industry*: aluminum, antimony, arsenic, barium, beryllium, bismuth, cadmium, calcium, carbon, cerium, chromium, cobalt, copper, gallium, germanium, gold, indium, iridium, iron, lanthanum, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, osmium, phosphorus, platinum, polonium, praseodymium, rhenium, rhodium, selenium, silicon, sodium, strontium, sulfur, tantalum, tellurium, thallium, tin, titanium, tungsten, vanadium, zinc, and zirconium.

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CHAPTER 1.26

Cobalt-base Alloys

Erwin Eichen and J. H. Jackson

REACTOR APPLICATION

With the advent of jet engines and gas and steam turbines, there arose a need for metals to withstand higher and higher temperatures. The first alloys used for this purpose were stainless steels. Because stainless steels are unable to withstand fluctuating stress and shock at high temperatures, however, the so-called "superalloys" or "super-steels" were developed for this purpose. The cobalt-base alloys are one type of "superalloy."

The urgent need for high-temperature alloys of this type during World War II, led to the development of these alloys on an empirical basis. That is, an alloy was developed for a specific elevated-temperature use without investigating its properties. Many alloys (some of which are now obsolete and no longer made commercially) were therefore developed about which little was known save for room- and elevated-temperature strengths. Table 1.26.1 lists chemical compositions of some representative, currently-available alloys.

During the past few years, much work has been done on determining the physical constants of cobalt-base alloys as well as on establishing fabrication procedures and heat treatments to obtain optimum properties.

Under the severe operating conditions of high-temperature nuclear reactors, alloys of the "superalloy" (cobalt-base) classification will have utility. They may be used to contain, protect, and support fissionable material. Because of their superior elevated-temperature properties, the significance of the high thermal-neutron absorption of cobalt is somewhat mollified. At higher energies, the cross section of cobalt is comparable with that of molybdenum and is a less important consideration. However, a high residual activity is an undesirable characteristic of cobalt-base alloys. Cobalt-base alloys are presently used in reactors in certain wear-resistant components, such as guides for control rods.

AVAILABILITY AND COST

The availability of cobalt-base alloys is dependent on the availability of the various alloying elements which make up the alloys.

COBALT

At present, there is a critical shortage of cobalt. However, as a result of increased production and recovery of cobalt, it is expected that by 1954 there will no longer be any shortage if there is no drastic increase in the amount of this metal used.

Table 1.26.1 — Chemical Composition of Cobalt-base Alloys

Alloy designation §	Producer	Chemical composition, %											
		Co	Cr	Ni	C	Fe	Mo	W	Nb	Ti	Si	Mn	Other
HS-6*	Haynes-Stellite	65.0	27.0	...	1.25	4.0	2.7
HS-21 (Vitalium)*	Haynes-Stellite	65.0	25.0	2.0	0.25	1.0	5.0	0.60	0.60	...
HS-23 (61)*	Haynes-Stellite	65.0	25.0	2.0	.40	1.0	...	6.060	.30	...
HS-25†	Haynes-Stellite	51.0	20.0	10.0	.12	1.0	...	15.0	1.00	1.50	...
HS-27 (6059)*	Haynes-Stellite	34.0	25.0	32.0	.40	1.0	6.0	0.60	0.60	...
HS-30 (422-19)*	Haynes-Stellite	51.0	24.0	16.0	.40	1.0	6.060	.60	...
HS-31 (X-40)*	Haynes-Stellite	55.0	25.0	10.0	.40	1.0	...	8.060	.60	...
HS-36*	Haynes-Stellite	44.0	18.5	10.0	.40	2.0 max	...	14.550	1.25	...
K-42-B*	Westinghouse Electric Corporation	22.0	18.0	43.0	.05	13.0	2.5	.70	0.70	0.6 Al
MIT-J*	Massachusetts Institute of Technology	60.0	23.0	6.0	.70	...	6.0	1.00	2.0 Ta
N-153*	Haynes-Stellite*	13.0	16.0	15.0	.15	Bal.	3.0	2.0	1.0	...	0.50	1.50	0.12 N
N-155 (Multimet)†	Haynes-Stellite*	20.0	20.0	20.0	.15	31.0	3.0	2.0	1.050	1.50	.15 N
Nimonic 90†	International Nickel Company	20.0	19.0	50.0	.10	4.0	2.4	1.50	1.00	1.2 Al
Refractaloy 26†	Westinghouse Electric Corporation	20.0	18.0	37.0	.05	17.0	3.0	3.0	0.70	0.70	0.2 Al
Refractaloy 70†	Westinghouse Electric Corporation	30.0	20.0	20.0	.05	15.0	8.0	4.020	2.00	...
Refractaloy M284†	Westinghouse Electric Corporation	30.0	20.0	20.0	.10	15.5	8.0	4.025	2.00	...
S-497†	Allegheny-Ludlum Steel Corporation	19.0	13.6	19.5	.40	Bal.	4.0	4.0	4.050	0.60	...
S-590†	Allegheny-Ludlum Steel Corporation	20.0	20.0	20.0	.40	24.0	4.0	4.0	4.070	1.50	...
S-816†	Allegheny-Ludlum Steel Corporation	44.0	20.0	20.0	.40	3.0	4.0	4.0	4.070	1.50	...
Ticonium†	Allegheny-Ludlum Steel Corporation	32.5	27.5	31.5	.20	1.5	5.040	0.70	...
Timken X†	Timken Roller Bearing Company	30.7	16.8	28.6	.15	Bal.	10.575	1.50	...
X-41*	General Electric Company	Bal.	25.0	8.2	.50	7.550	0.50	0.19 N
X-50*	Haynes-Stellite	40.7	22.6	20.0	.75	12.250	.60	...
8658-1*	Battelle Memorial Institute	20.0	19.0	15.0	.35	...	2.8	...	0.70	...	1.7	2.0	0.50 Ta
8658-2*	Battelle Memorial Institute	19.7	18.7	15.0	.35	...	2.7	...	1.25	...	1.7	2.0	.90 Ta
8659*	Battelle Memorial Institute	19.7	17.6	25.0	.40	...	3.7	...	1.50	...	1.8	2.0	1.0 Ta

* Available only in cast form

† Primarily available in wrought form

‡ Cast or wrought

§ The terms Haynes, Haynes-Stellite and Multimet are trademarks of the Union Carbide and Carbon Corporation

OTHER ALLOYING ELEMENTS

The availability of the other alloying elements used in these alloys can be found in the chapters on stainless steels, molybdenum, and tungsten. The cost of cobalt-base alloys is dependent on the chemical composition. In general, it might be said that the cost of the alloys increases as the cobalt content increases. The June 1952 price of cobalt was approximately \$2.40/lb.

PHYSICAL AND CHEMICAL CONSTANTS

The physical constants of cobalt-base alloys depend upon the chemical composition of the alloy. It is also quite probable that the physical constants of each alloy will vary slightly from heat to heat depending on the actual alloy content.

The thermal cross section of these alloys can be computed from the thermal cross sections of the various alloying elements by the law of mixtures.

Table 1.26.2 lists the available physical constants of a number of cobalt-base alloys.

MECHANICAL PROPERTIES

The strength and ductility of the various cobalt-base alloys are dependent on their compositions. Other factors which also affect these properties are the prior thermal-mechanical history as well as testing temperature and conditions. Table 1.26.3 gives the room-temperature mechanical properties of a number of cobalt-base alloys under various conditions. Figures 1.26.1 through 1.26.29 give the elevated-temperature properties of many of the cobalt-base alloys.

MELTING AND CASTING

MELTING

The melting procedures which are used for stainless steels can be easily adapted to cobalt-base alloys. However, the size of the heat of cobalt-base alloys is usually much smaller, varying from 35 to 2000 lb. The types of furnaces used are the carbon resistance, induction, and the basic direct or indirect arc.

CASTING TECHNIQUES

Two types of casting techniques are used for cobalt-base alloys. The first is the casting of ingots into permanent molds. This type of casting is done for materials which can be hot worked. The casting method is the same as that used for permanent molding stainless steels.

Because many of the cobalt-base alloys cannot be easily or economically worked, it is necessary to cast these alloys to shape. This is done by the use of a precision or investment casting technique. This type of casting involves the use of a pattern which is an exact replica of the part. These patterns are made from either a low-melting wax or plastic which can be melted without leaving any residue. A mold is then made using a fine-grained refractory such as silica flour. The mold is heated to burn out the pattern and then fired.

The metal is cast into the mold cavity under low pressure, or by use of centrifugal casting methods. The surface smoothness of the casting depends on the fineness of the refractory. For small castings, certain dimensions can be held to 0.003 in./in.

FORMING AND FABRICATION

HOT WORKING

In general, for cobalt-base alloys, hot working is usually limited to forging and rolling. The following alloys are considered to be forgeable and are usually used in the wrought condition: Multimet, Refractaloy 26, Refractaloy 70, HS-25, S-590, and S-816. The forging and rolling techniques used for these alloys are similar to those used for austenitic stainless steels. However, because of their greater strength at elevated temperatures, ma-

Table 1.26.2 — Physical Constants of Various Cobalt-base Alloys

Alloy Designation	Density, gm/cm ³	Melting Point, °F	Specific heat		Mean thermal-expansion coefficient, per °F × 10 ⁶							Thermal conductivity, Btu/(hr)(ft)(°F)					Electrical resistivity, μohm-cm			
			77°-572°F	77°-932°F	77°-1292°F	70°-600°F	70°-800°F	70°-1000°F	70°-1200°F	70°-1500°F	70°-1600°F	392°F	572°F	752°F	932°F	1112°F	81°F	990°F	1302°F	1505°F
HS-6	8.38	2327	0.101	8.03	8.18	8.32	8.65	...	9.30	91.0
HS-21 (Vitalium)	8.30	7.93	7.96	8.18	8.38	8.68	...	1212	1332	2652	1584	1704
HS-23 (61)	8.54	7.64	7.96	8.18	8.48	9.24	...	1284	1464	1500	1572	1764
HS-25	9.15	2750	7.61	8.28	8.30	8.55	9.11	88.7
HS-27	8.21	7.53	7.79	8.04	8.29	8.67	8.84	1176	1284	1380	1512	1644
(6059)
HS-30	8.31	7.70	7.86	7.91	8.07	8.42	8.54
(422-19)
HS-31	8.61	7.94	8.08	8.39	8.75	9.19	9.19	1236	2652	1464	1608	1824
(X-40)
HS-36	9.04	2535
N-153	8.15	9.21	9.27	9.51	9.64	9.78
N-155 low carbon	8.20	8.70	8.89	9.10	9.40	9.77	...	1212	1320	1440	1548	1668
(Multimet)
Nimonic 90	8.27	7.1	7.4	7.7	8.1	8.9	9.2	1044	2400	...	115
...
Refractaloy	8.53	7.68	7.96	8.23	8.42	8.93	9.10
M284
S-497	8.57	7.92	8.00	8.26	8.50	8.80
S-590	8.31	2400- 2500	0.10	0.10	0.11	8.47	8.43	8.54	8.61	8.94	9.20	1236	1332	...	1596	1728
S-816	8.66	2350- 2450	.09- 0.10	.10	.12	9.85	9.70	9.50	9.79	9.80	9.90	1320	1428	...	1704	1860	93.0	109.3	111.4	113.0
X-50	8.86	7.88	7.98	8.18	8.43	8.79

Table 1.26.3—Room-temperature Mechanical Properties of Various Cobalt-base Alloys

Alloy Designation	Condition	Ultimate strength, lb/sq in.	Proportional limit, lb/sq in.	Yield strength, (0.2% Offset) lb/sq in.	Elongation, %	Reduction of area, %	Modulus of elasticity, 10^6 lb/sq in.	Hardness, Rockwell "A"	Charpy impact strength, ft-lb
HS-21	As cast	101,300	63,500	82,300	8.2	9.0	36.0	65.0	2.9
	Aged 50 hr at 1350°F	124,500	64,000	110,400	1.7	3.6	29.0	69.5	...
HS-23	As cast	111,000	52,400	86,800	8.7	12.3	29.0	65.0	2.4
	Aged 50 hr at 1350°F	132,700	57,000	121,000	2.5	4.0	32.2	71.5	...
HS-25	0.050 Sheet	150,000	...	108,500	40.0
HS-27	As cast	90,800	34,900	65,200	12.7	13.8	28.0	61.0	2.3
	Aged 50 hr at 1350°F	100,500	39,000	70,300	7.7	8.4	28.0	67.5	...
HS-30	As cast	96,900	59,000	81,100	10.0	11.3	27.0	65.5	1.5
	Aged 50 hr at 1350°F	119,700	64,500	104,900	2.7	5.6	25.0	71.0	...
HS-31	As cast	113,000	51,300	79,500	8.0	9.5	36.0
	Aged 50 hr at 1350°F	128,300	68,000	112,700	2.0	2.9	27.0
HS-36	As cast	100,000	...	95,000	5.5	8.5
	Aged 16 hr at 1350°F	125,000	...	107,500	1.7	4.0
N-155	Forged	117,600	...	71,500	30.0	48.0	30.8
	Sheet	116,000	...	57,000	43.0	49.0
X-40	As cast	101,000	...	58,000	30.5	21.0
	As cast	101,000	...	74,100	11.0	14.0	...	64.0	2.3
S-616	As cast	100,000	6.0	7.4
	As rolled	175,000	...	73,000	39.0	45.0	35.2	...	9.0

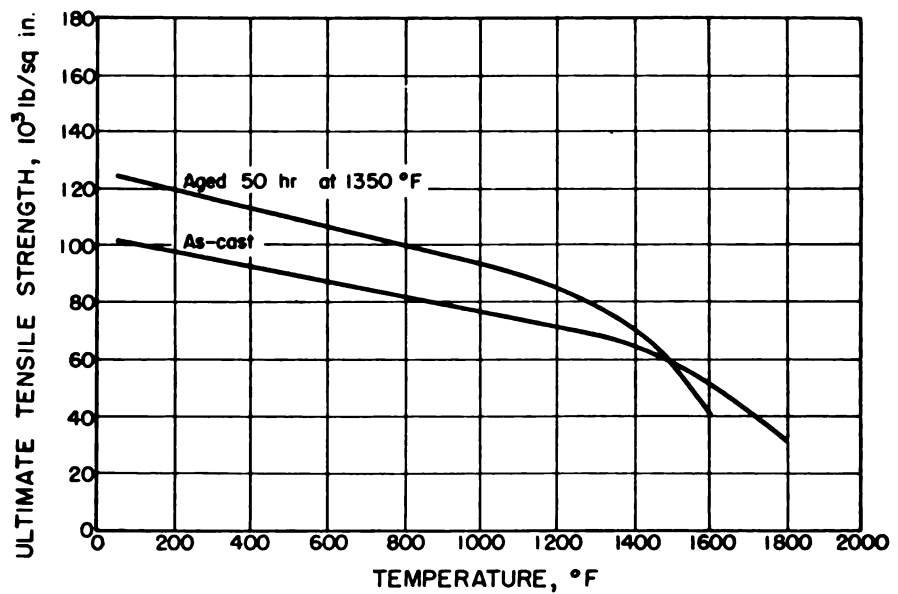


Fig. 1.26.1 — Ultimate Strength of Haynes Alloy 21 at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

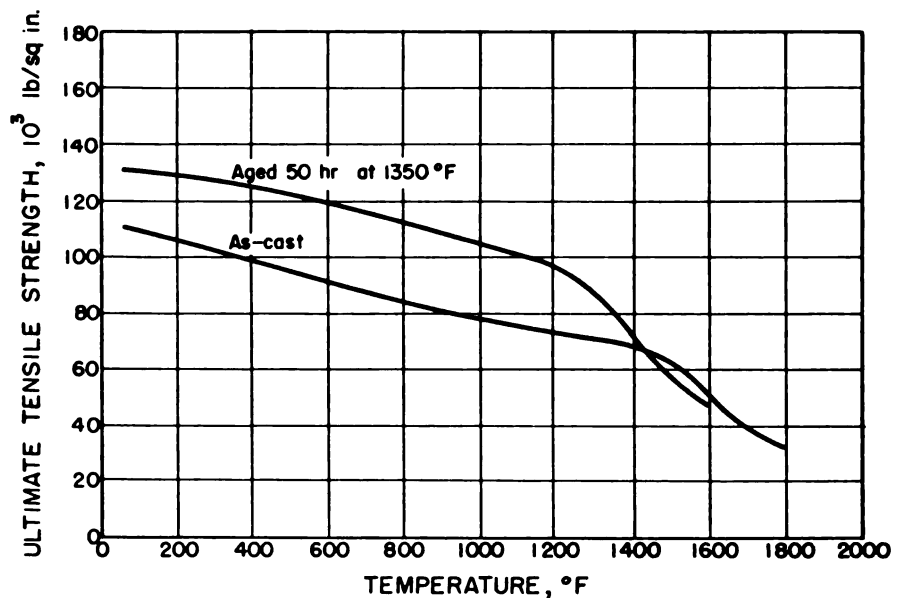


Fig. 1.26.2 — Ultimate Strength of Haynes Alloy 23 at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

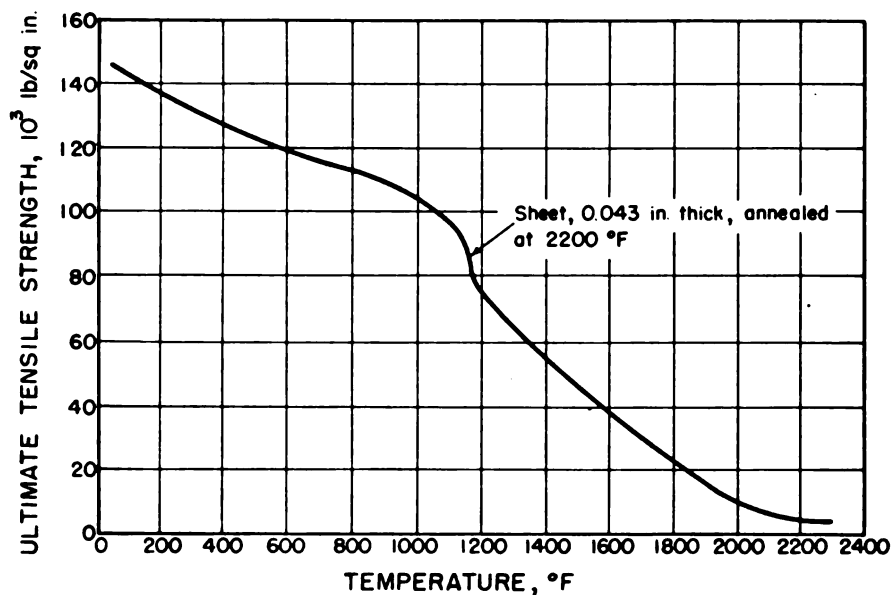


Fig. 1.26.3—Ultimate Strength of Haynes Alloy 25 at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

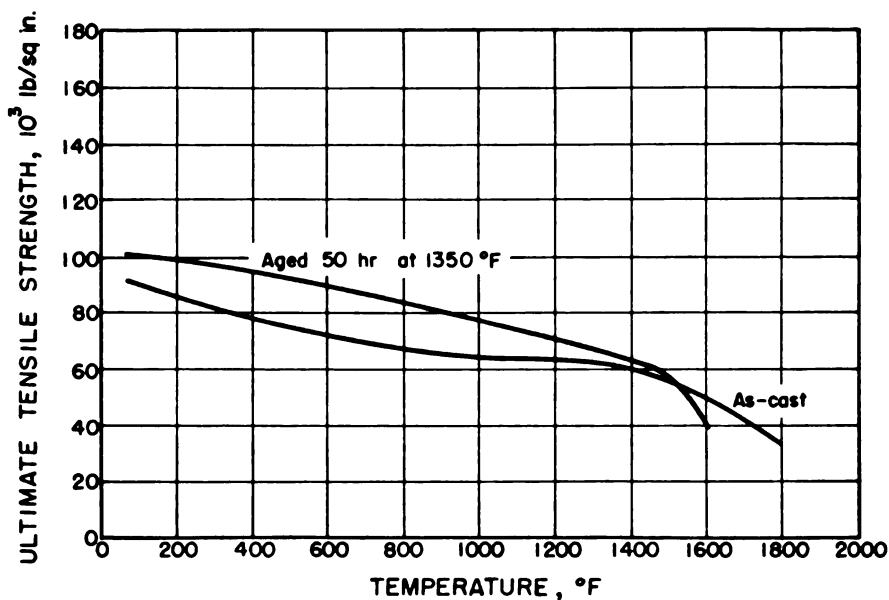


Fig. 1.26.4—Ultimate Strength of Haynes Alloy 27 at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

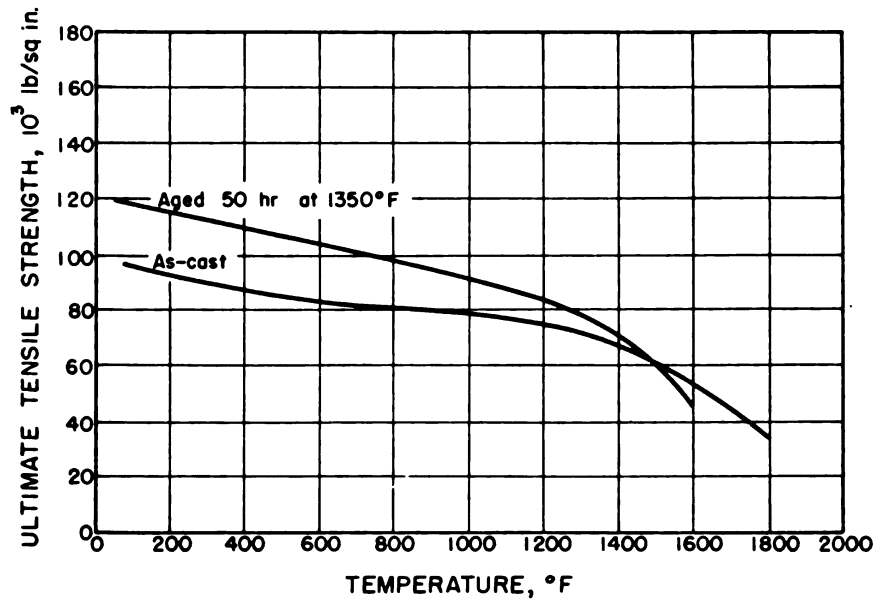


Fig. 1.26.5—Ultimate Strength of Haynes Alloy 30 at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

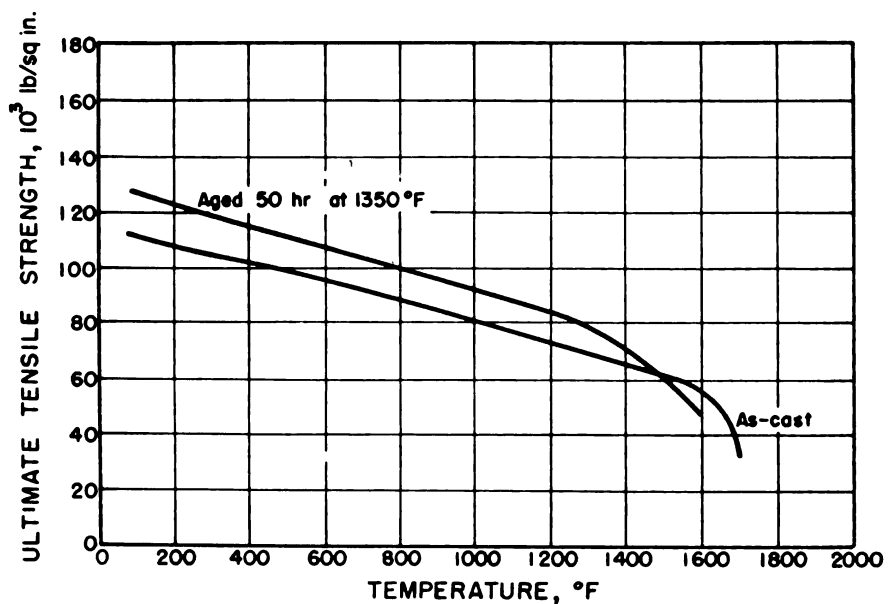


Fig. 1.26.6—Ultimate Strength of Haynes Alloy 31 at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

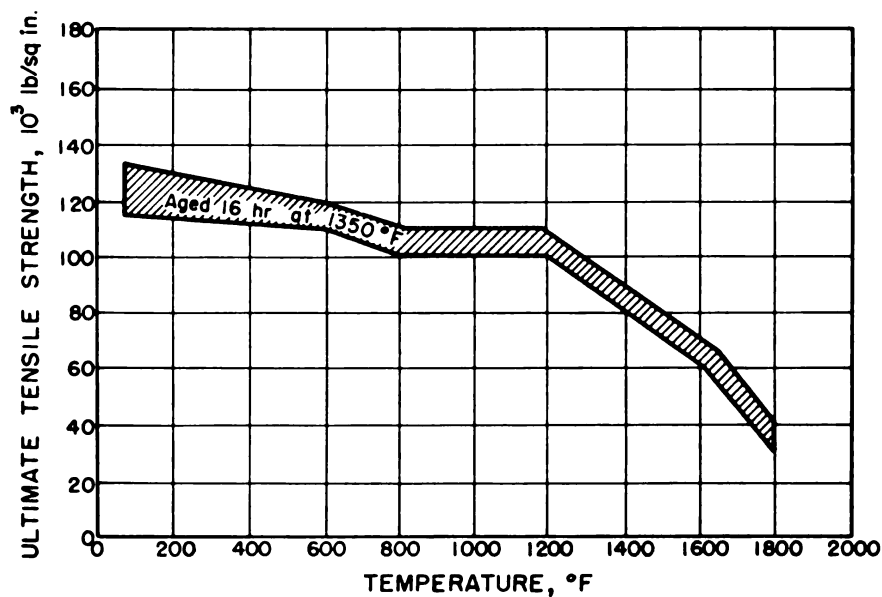


Fig. 1.26.7—Ultimate Strength of Haynes Alloy 36 at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

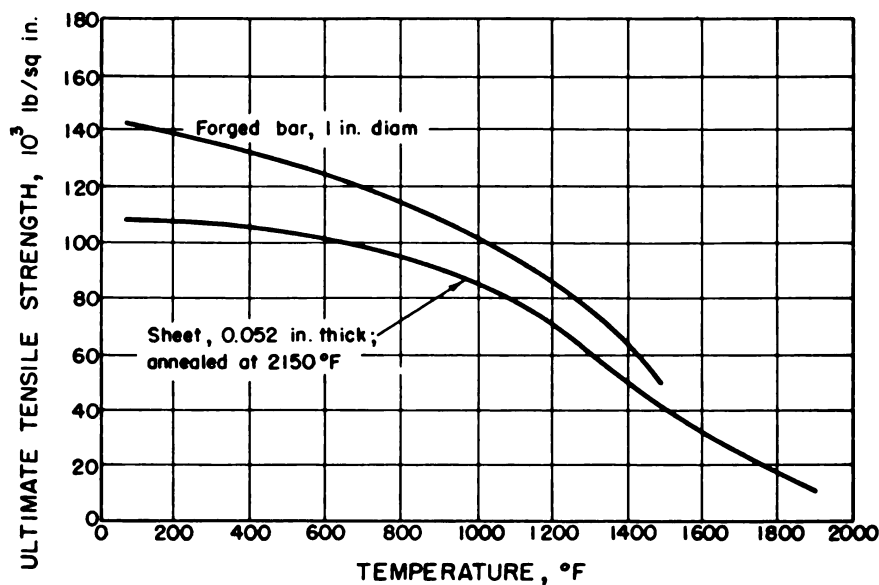


Fig. 1.26.8—Ultimate Strength of Haynes Wrought Multimet at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

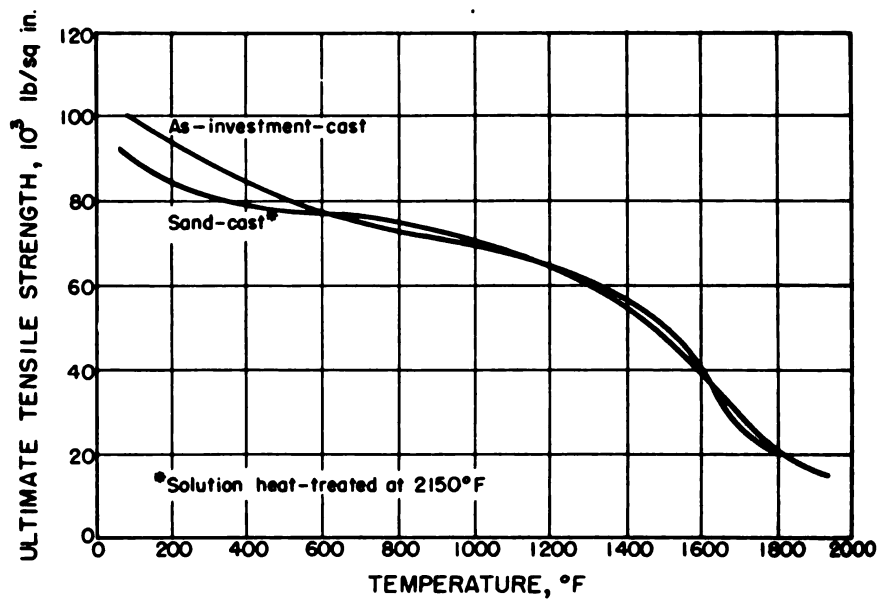


Fig. 1.26.9—Ultimate Strength of Haynes Low-carbon Multimet at Various Temperatures. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

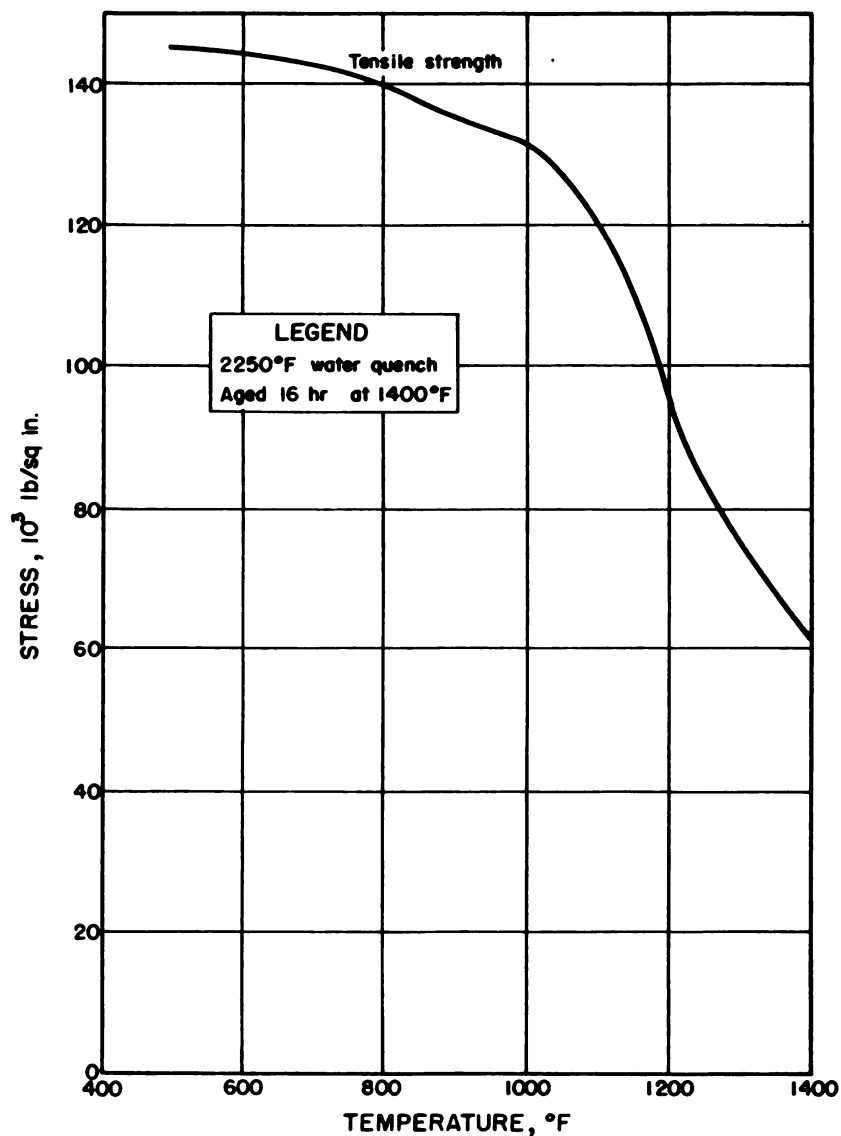


Fig. 1.26.10 —Tensile Strength of S-590 Alloy at Various Temperatures. Constructed from Data Supplied by Allegheny-Ludlum Steel Corporation.

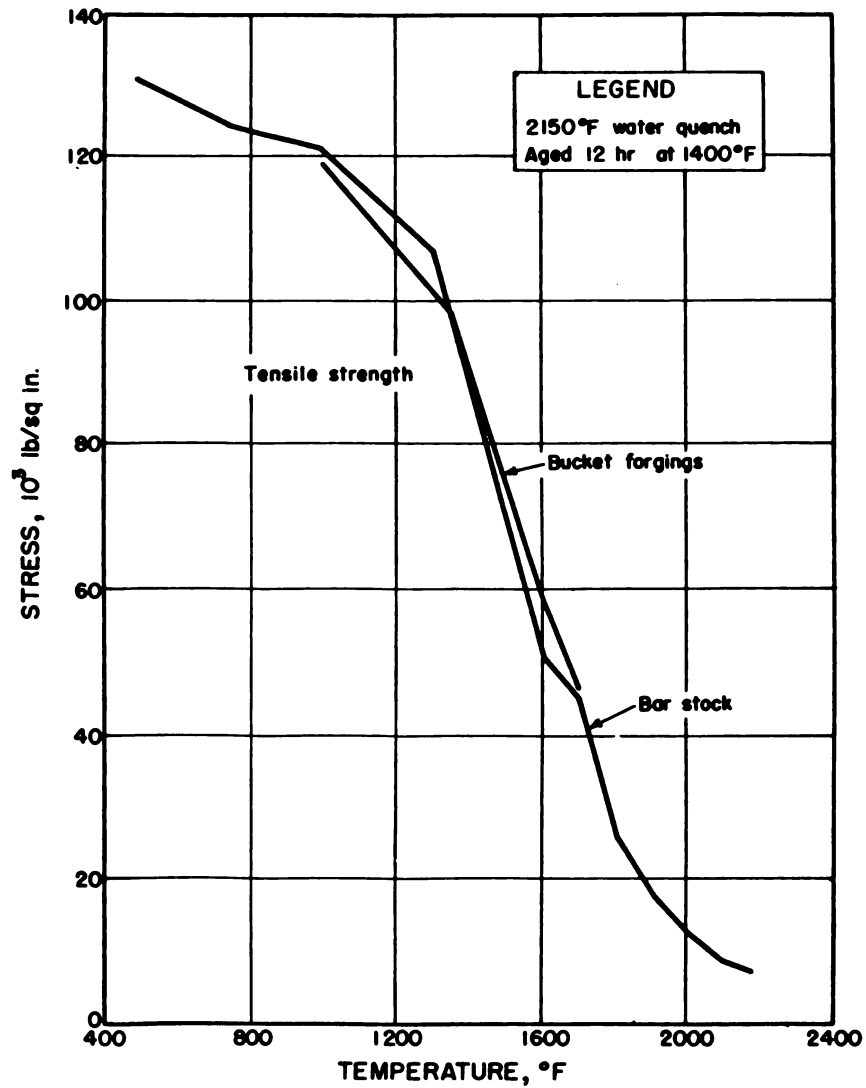


Fig. 1.26.11 —Tensile Strength of S-816 Alloy at Various Temperatures. Constructed from Data Supplied by Allegheny-Ludlum Steel Corporation.

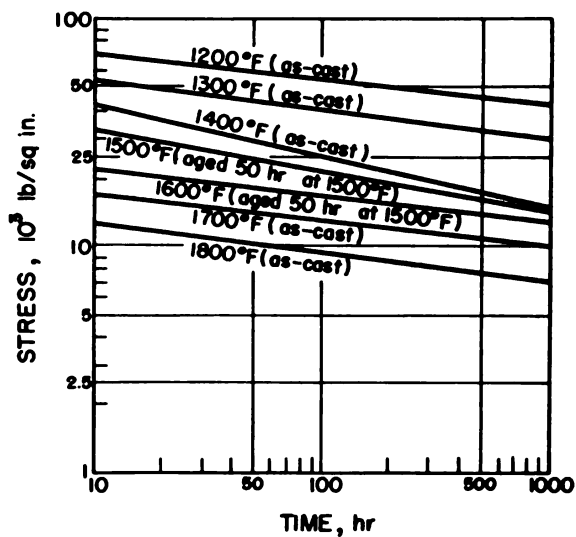


Fig. 1.26.12—Stress-rupture Data for Haynes Alloy 21. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

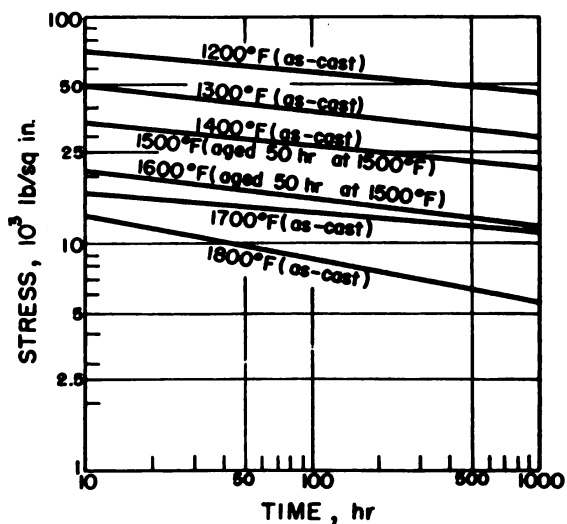


Fig. 1.26.13—Stress-rupture Data for Haynes Alloy 23. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

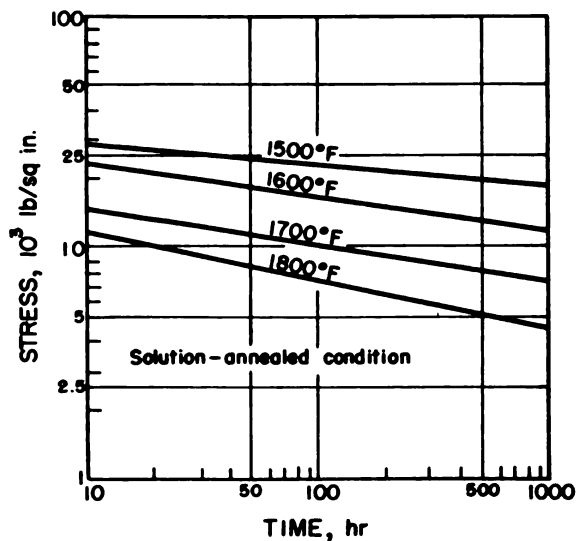


Fig. 1.26.14—Stress-rupture Data for Haynes Alloy 25. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

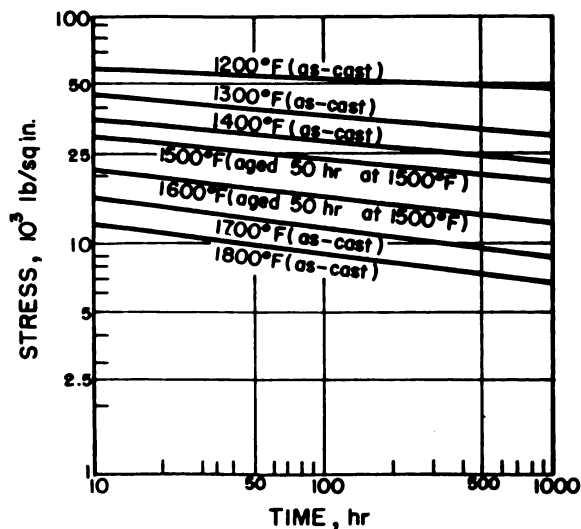


Fig. 1.26.15—Stress-rupture Data for Haynes Alloy 27. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

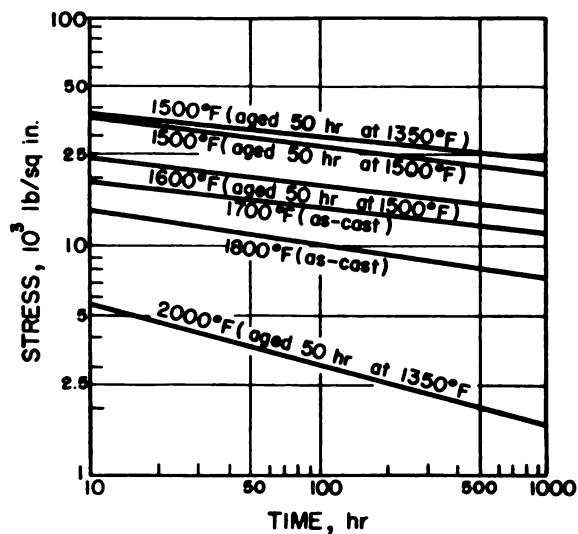


Fig. 1.26.16 —Stress-rupture Data for Haynes Alloy 30. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

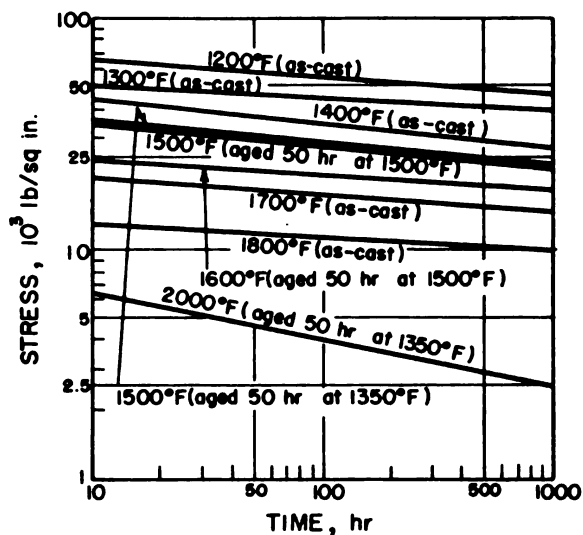


Fig. 1.26.17 —Stress-rupture Data for Haynes Alloy 31. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

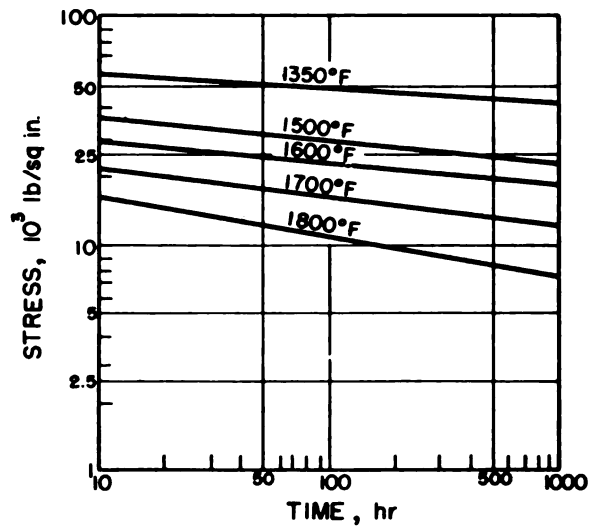


Fig. 1.26.18 — Stress-rupture Data for Haynes Alloy 36. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

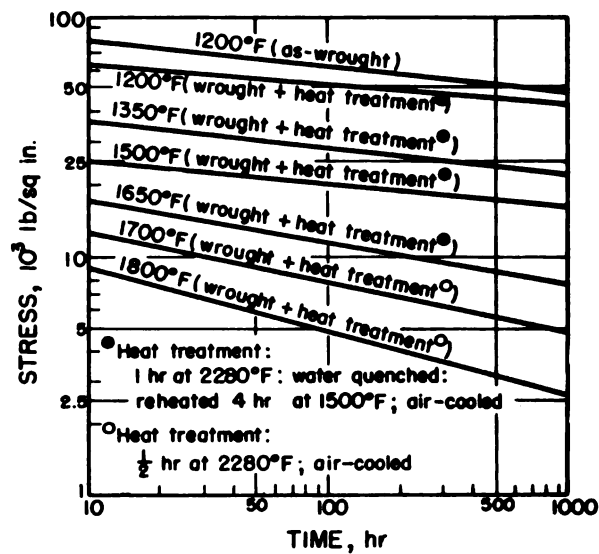


Fig. 1.26.19 — Stress-rupture Data for Haynes Wrought Multimet. Reprinted from Haynes Alloys for High-temperature Service, Haynes Stellite Co., Kokomo, Ind.

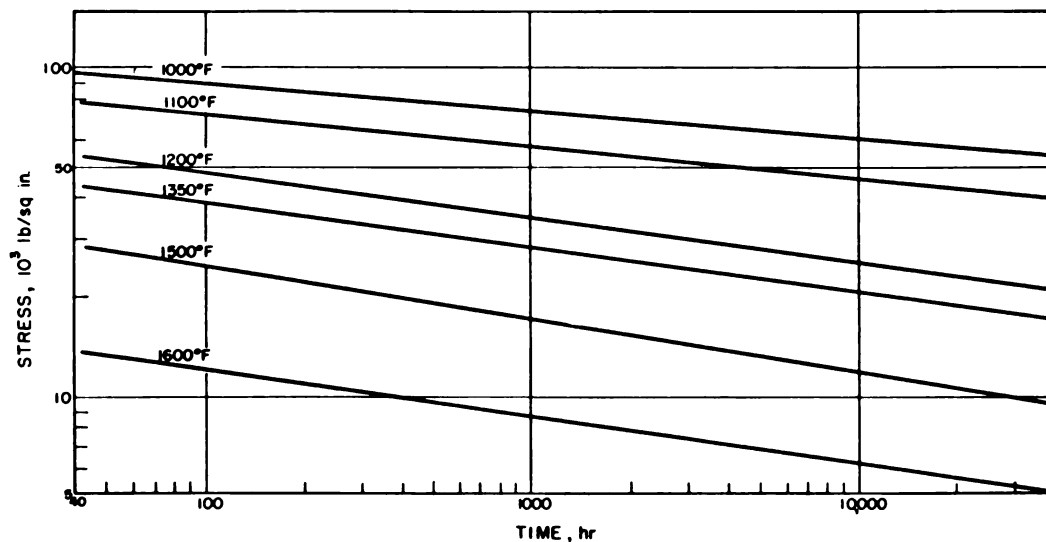


Fig. 1.26.20 — Stress-rupture Data for Alloy S-590. Constructed from Data Supplied by Allegheny-Ludlum Steel Corporation.

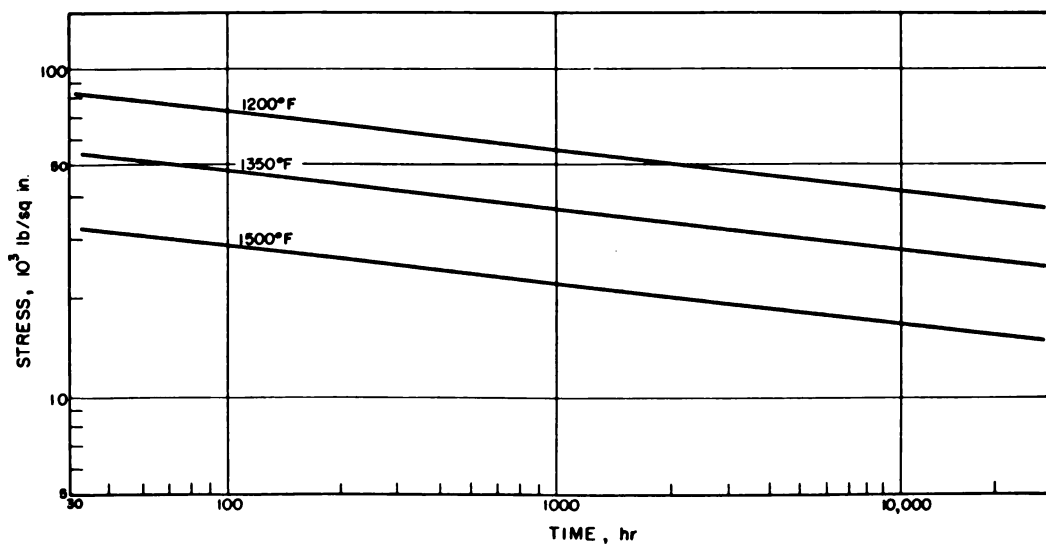


Fig. 1.26.21 — Stress-rupture Data for Alloy S-816. Constructed from Data Supplied by Allegheny-Ludlum Steel Corporation.

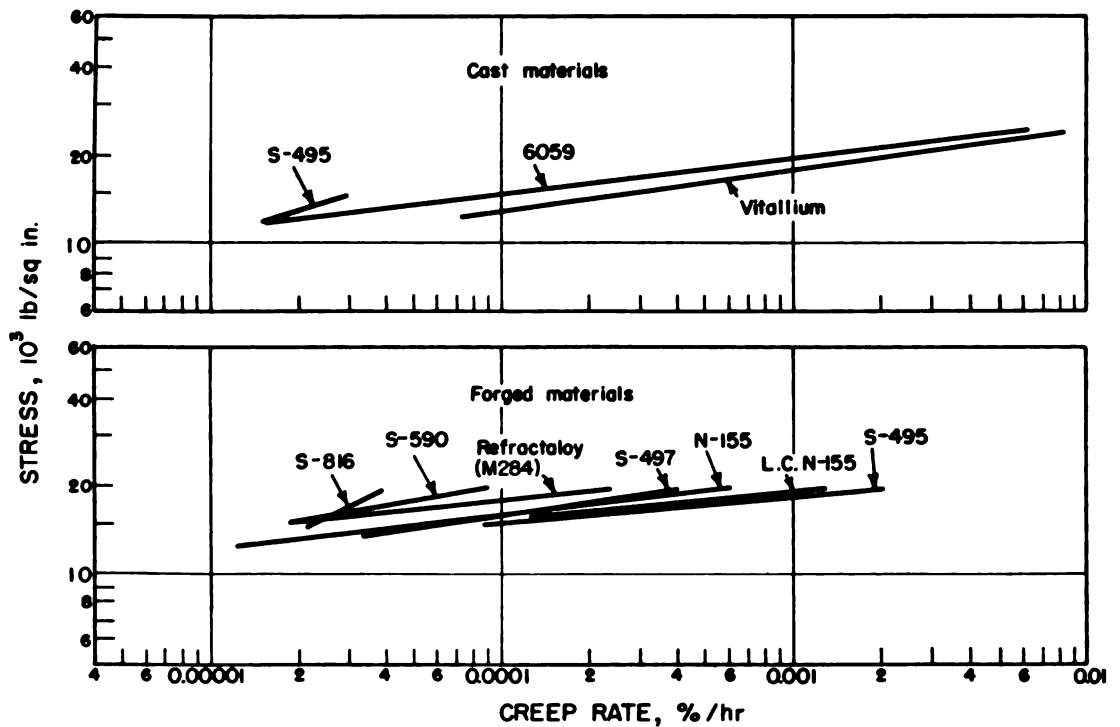


Fig. 1.26.22 —Stress Versus Minimum Creep Rate for Alloys 6059, N-155, S-495, S-497, S-590, S-816, Refractaloy M284, and Vitallium (Haynes 21) at 1350°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

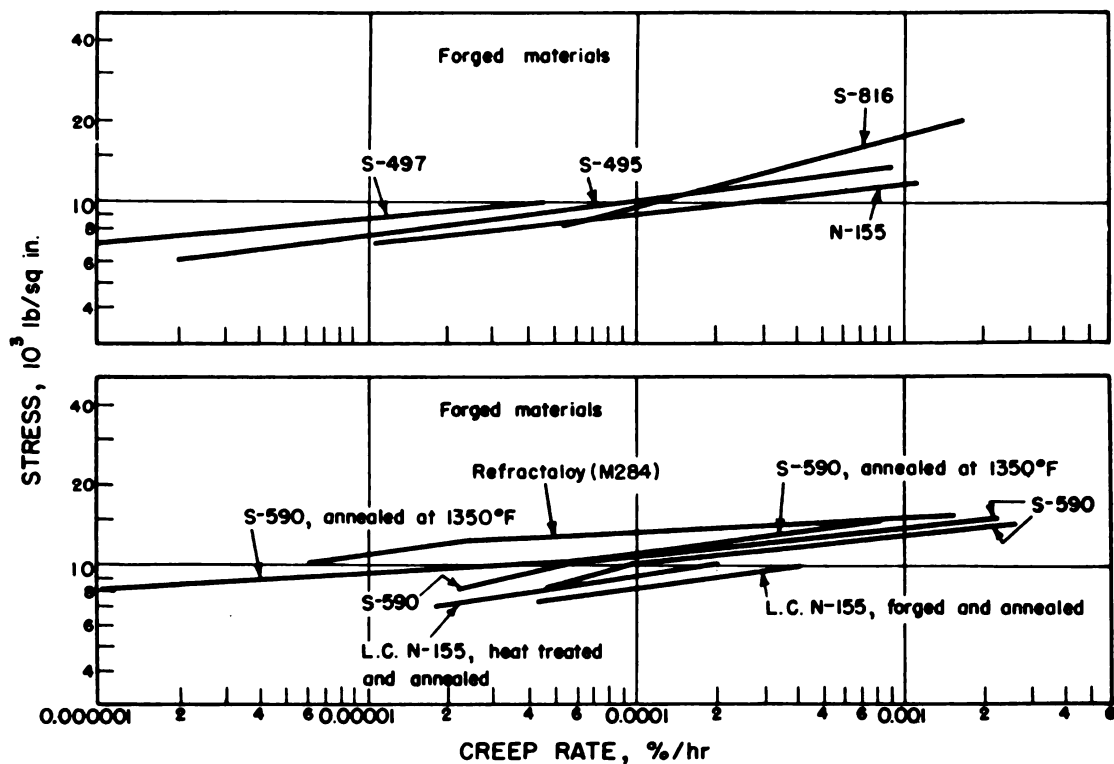


Fig. 1.26.23 — Stress Versus Minimum Creep Rate for Alloys N-155, S-495, S-497, S-590, S-816, and Refractaloy M284 at 1500°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

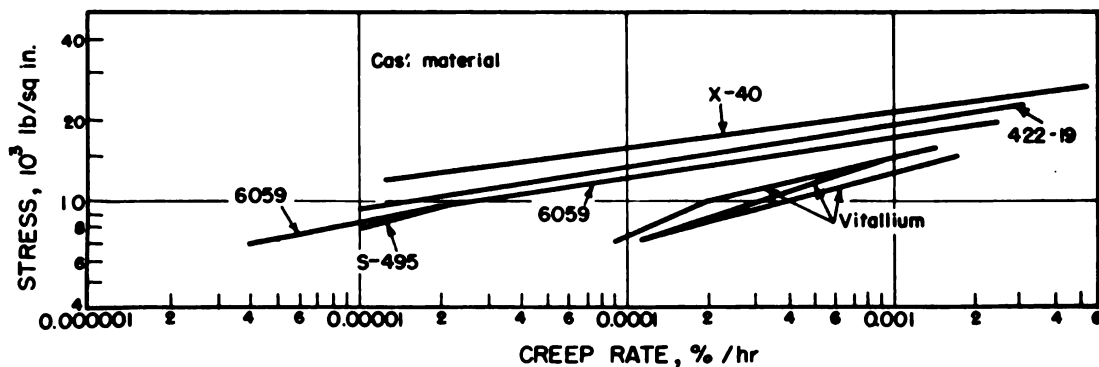


Fig. 1.26.24 — Stress Versus Minimum Creep Rate for Alloys 422-19, 6059, S-495, X-40, and Vitallium at 1500°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

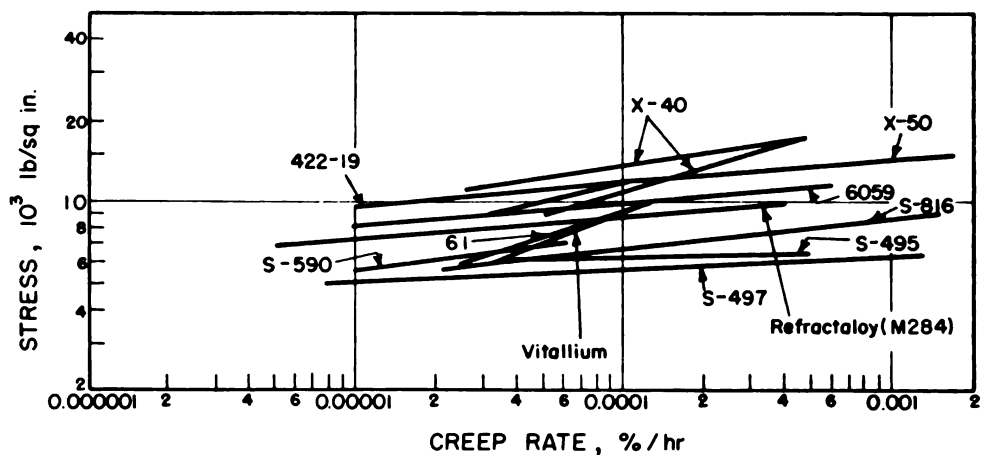


Fig. 1.26.25 — Stress Versus Minimum Creep Rate for Alloys 61, 422-19, 6059, S-495, S-497, S-816, X-40, X-50, Refractaloy M284, and Vitallium (Haynes 21) at 1600°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

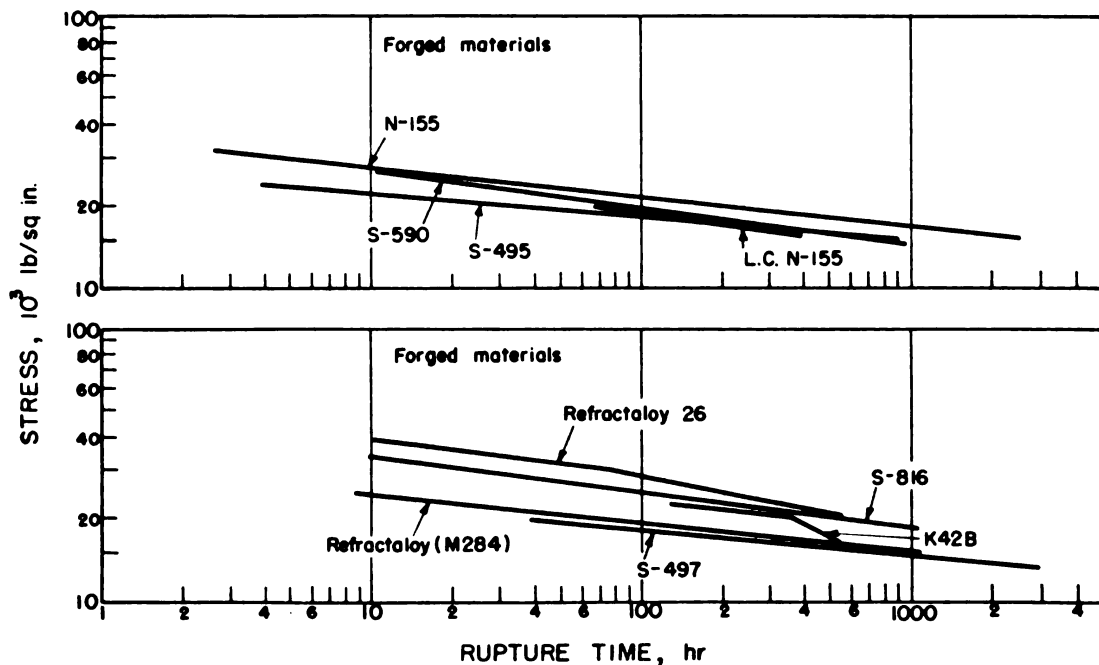


Fig. 1.26.26 — Stress-rupture Data for K42B, N-155, S-495, S-497, S-590, S-816, Refractaloy M284, and Refractaloy 26 at 1500°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

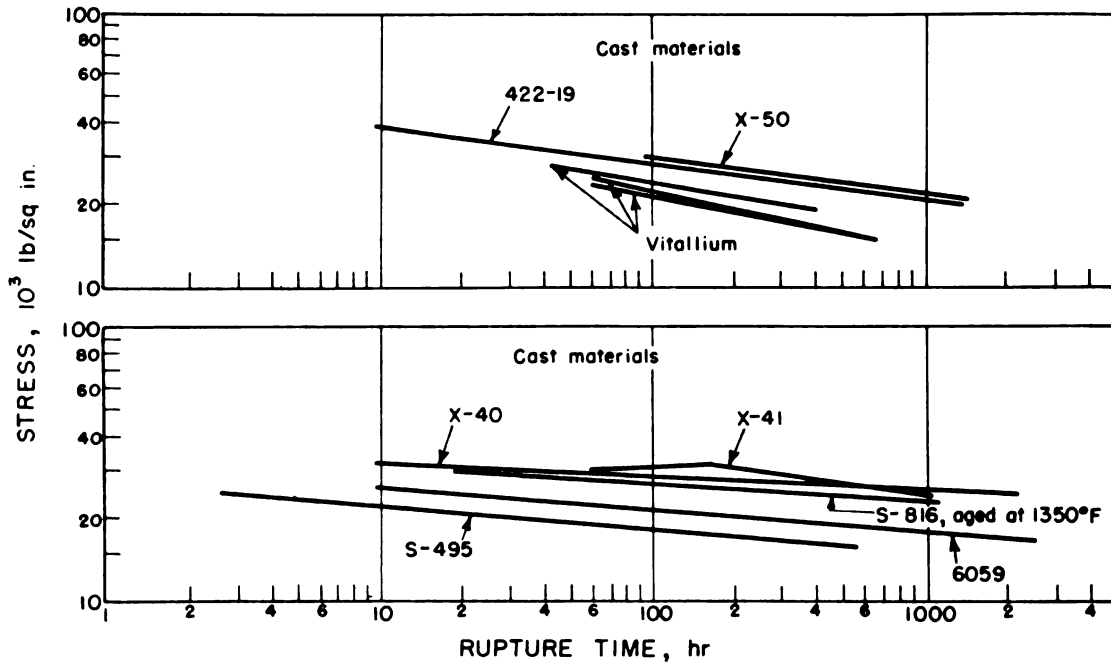


Fig. 1.26.27—Stress-rupture Data for 422-19, 6059, S-495, S-816, X-40, X-41, X-50, and Vitallium (Haynes 21) at 1500°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

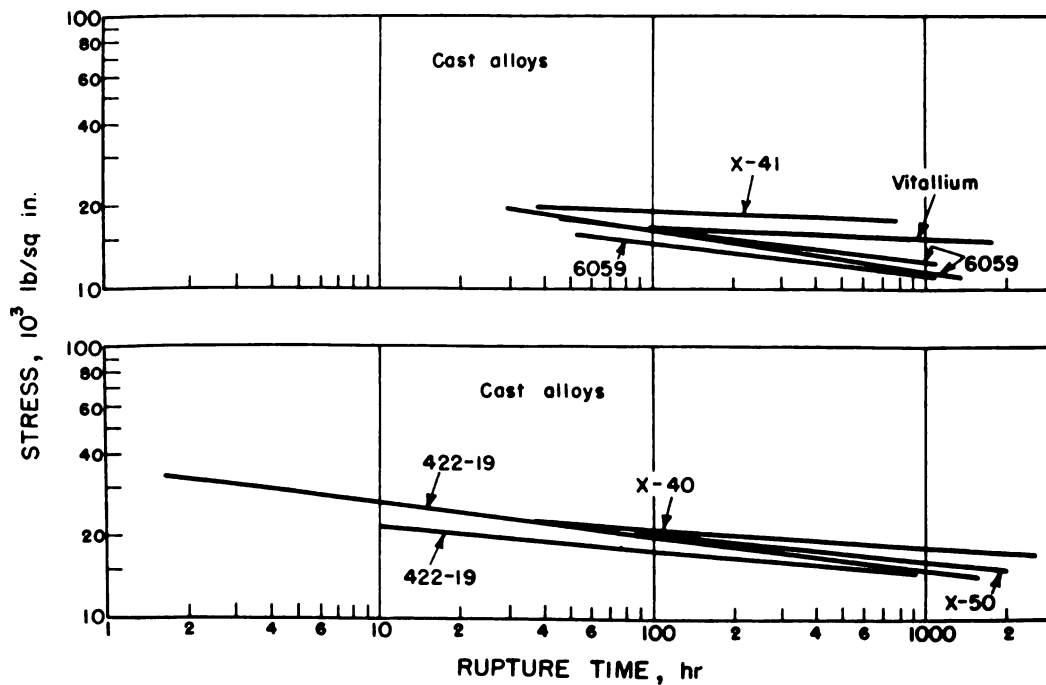


Fig. 1.26.28—Stress-rupture Data for 422-19, 6059, X-40, X-41, X-50, and Vitallium (Haynes 21) at 1600°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

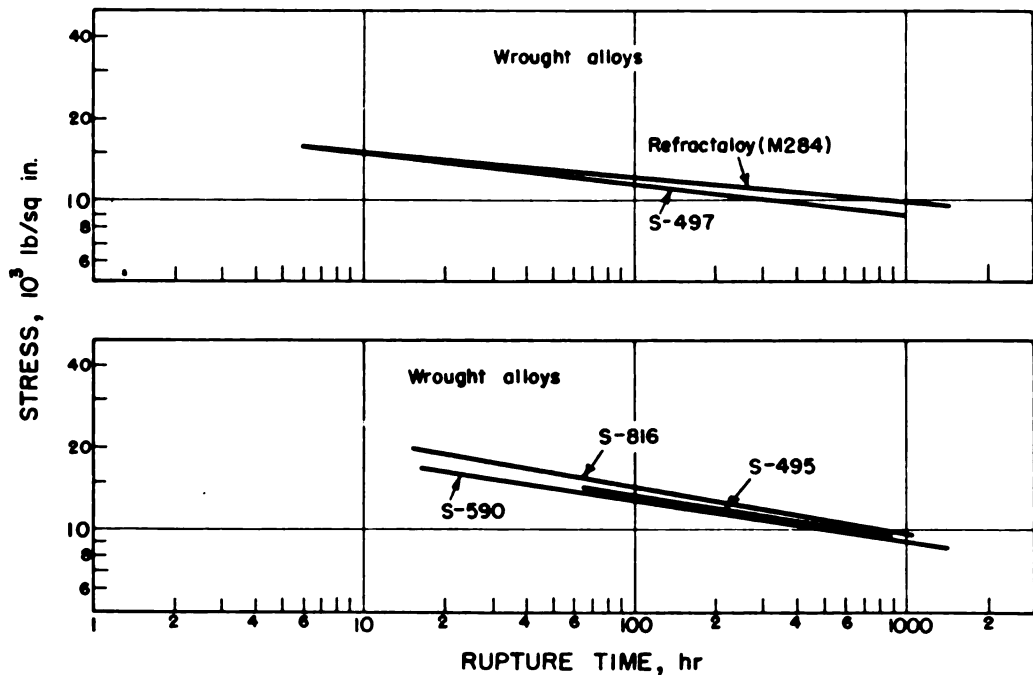


Fig. 1.26.29 — Stress-rupture Data for S-495, S-497, S-590, S-816, and Refractaloy M284 at 1600°F. Reprinted from ASTM Symposium on Materials for Gas Turbines.

chines of greater capacity, smaller reductions, and more reheats are needed than for stainless steels. The forging temperature for these alloys is from 2100° to 2250°F with liberal soaking times. Precision bucket forgings have been made to close tolerances by means of drop forging.

POWDER METALLURGY

As yet, practically no effort has been made in applying powder metallurgical processes to cobalt-base alloys. However, several very interesting possibilities exist. In the first place, component parts can be made to size to eliminate any forming and machining difficulties. The second possibility is that component parts could be made with controlled amounts of porosity. This would serve two purposes. The first is that it would increase the strength-to-weight ratio of the part by reducing its weight. The second is that it might be possible to pass a cooling media through the part and thereby actually reduce the operating temperature of the part. Some work will have to be done to determine the feasibility of fabricating cobalt-base alloy parts by powder metallurgical means.

JOINING

SOLDERING

Soldering is not used as a means of joining cobalt-base alloys.

BRAZING

Brazing techniques have been successfully applied to cobalt-base alloys. Furnace brazing in a controlled atmosphere is preferred because of uniform results. When braz-

ing, care must be taken to avoid excess age hardening by holding too long in the critical temperature range around 1500°F. Brazing as a means of joining these alloys is limited to the elevated-temperature strength of the joint.

WELDING

Welding the cobalt-base alloys presents special problems because of the inherent characteristics of these metals. However, with care, these alloys can be successfully welded. In general, the procedure for welding these alloys is similar to that used for welding austenitic stainless steels. Rapid travel and minimum current consistent with the size of the part should be used to avoid overheating and a large heat-affected zone. Haynes Alloys 1, 6, and 21, Hastelloy B, Hastelloy C, Multimet, and stainless steel electrodes have been successfully used in the welding of cobalt-base alloys.

The following methods can be used to weld cobalt-base alloys: resistance welding (spot, roller-seam, and flash welding), submerged arc (Unionmelt), metallic-arc, atomic hydrogen, Heliarc, Argonarc, and oxyacetylene.

HARD-FACING

Cobalt-base alloys are often used as hard-facing materials. Representative cobalt-base alloy used for hard facings are Haynes Stellites 1, 6, 12, and 21, and Hastelloy C. These alloys may be applied by any of the standard hard-facing techniques, such as oxyacetylene, metallic-arc, atomic-hydrogen, and argon-arc. In applying such hard-facing alloys, care should be exercised to prevent dilution of the hard-facing material by the base metal.

MACHINING

In general, the cobalt-base alloys are machinable. However, it is necessary to use slower speeds and lighter feeds than are used with austenitic stainless steels. Because of the great tendency for these alloys to work harden, a positive cut should be maintained at all times to prevent the surface from work hardening.

HEAT TREATMENT

FULL-ANNEAL

In order to full-anneal the cobalt-base alloys, these alloys must be heated into the temperature range 2100° to 2250°F. As yet, there are insufficient data available to give the optimum temperature for each alloy, but adequate ductility and machinability are obtained when alloys are heated into the above temperature range.

STRESS-RELIEF ANNEAL

For stress-relief annealing, cobalt-base alloys should be heat treated at a temperature of 2000° to 2100°F. Stress-relief heat treatments at temperatures lower than 2000°F will result in precipitation hardening in most of the alloys.

AGING HEAT TREATMENT

The majority of the cobalt-base alloys are susceptible to age or precipitation hardening. However, it is usually not necessary to preage these alloys because they have excellent elevated-temperature properties with aging. The aging actually supplements their elevated-temperature properties when these alloys are used in the temperature range 1300° to 2000°F.

CORROSION BEHAVIOR

The corrosion resistance of cobalt-base alloys is largely dependent on composition. As is the case with stainless steels, the oxidation resistance of these alloys is dependent on the chromium content. The alloys which contain chromium in amounts of approximately 20 percent or more have good oxidation resistance at temperatures as high as 1800° to 2000°F. In general, it might be said that the corrosion resistance of these alloys against all atmospheres encountered in gas-turbine or similar service is excellent up to 1500°F and good up to temperatures as high as 2000°F. It also appears that these alloys (or at least the Stellites) have good corrosion resistance to 500°F water. From preliminary information, it appears that the corrosion resistance of these alloys in liquid bismuth is poor: alloying takes place at 1400°F.

METALLOGRAPHY

The polishing techniques that are used for stainless steels work quite well for the cobalt-base alloys. Table 1.26.4 is a list of etchants which can be used with the cobalt-base alloys.

Table 1.26.4—List of Etchants Used for Cobalt-base Alloys
(From Haynes Alloys for High-temperature Service)

Etch	Remarks	Alloys Etched
(1) 5-10% HCl, electrolytic,	Use 2 dry cells in series; specimen anode, carbon-arc cathode; 1-5 sec	HS-21, HS-23, HS-27, HS-36
(2) a. HCrO ₄ , electrolytic, 2 gm CrO ₃ , 98 cc H ₂ O b. NaOH-KMnO ₄ , immersion, 1 part 20% KMnO ₄ , 1 part 8% NaOH	Same as (1) except 4 dry cells in series 5-10 sec; make up fresh each day	HS-21, HS-23, HS-27, HS-31
(3) 6% aqua regia, electrolytic	Same as (2); make up fresh each day	HS-21, HS-23
(4) 5% HCrO ₄ , electrolytic, 5 gm CrO ₃ , 95 cc H ₂ O	Same as (1)	HS-27, HS-30, HS-31, HS-36, N-155
(5) 4 parts HCl, 1 part 30% H ₂ O ₂	Immersion for 1-10 sec; make up fresh each day	HS-30
(6) 25 gm FeCl ₃ , 10 cc HCl, 100 cc H ₂ O	Immersion for 1-10 sec	N-155
(7) 6 parts HCl, 1 part H ₂ O ₂	Immersion for 10-20 sec	N-155
(8) HCl-H ₂ O ₂	Specimen is immersed in concentrated HCl, and H ₂ O ₂ is added dropwise until first sign of solution decomposition at which time specimen is removed	HS-25

SELECTED READING LIST

METALS AT HIGH TEMPERATURE, F. H. Clark, Reinhold Publishing Corporation, New York, New York, 372 pp, 1950.

PROPERTIES OF METALS AT ELEVATED TEMPERATURES, G. V. Smith, McGraw-Hill Book Company, New York, New York, 400 pp, 1950.

HAYNES ALLOYS FOR HIGH TEMPERATURE SERVICE, Haynes Stellite Corporation, Kokomo, Indiana, 96 pp, 1950.

TECHNICAL DATA ON ALLEGHENY-LUDLUM ALLOYS, Allegheny-Ludlum Steel Corporation, Pittsburgh, Pennsylvania.

CREEP STRENGTH OF ALLOYS, Battelle Memorial Institute, H. C. Cross, pp 134-187 in Materials Symposium Lectures, June 14-19, 1948, 532 pp, Secret, April 4, 1949.

HIGH TEMPERATURE PROPERTIES OF METALS, E. R. Parker, et al., American Society for Metals, Cleveland, Ohio, 176 pp, 1941.

SYMPOSIUM ON MATERIALS FOR GAS TURBINES, ASTM, Philadelphia, Penna., 1946.

Appendix

Table A.1—Selected Physical Constants of the Elements

Element	Thermal-neutron absorption cross section, barns/atom	Density near 20°C, gm/cm ³	Melting point, °C	Boiling point, °C	Specific heat near 20°C, cal/(gm)(°C)	Coefficient of linear thermal expansion near 20°C, per °C × 10 ⁻⁶	Thermal conductivity near 20°C, cal/(sec)(cm)(°C)	Electrical resistivity, microhm-cm	Crystal structure*	Goldschmidt atomic radius, Å
Actinium	1,600
Aluminum	0.215	2.699	600.2	2,327	0.215	23.8	0.503	2.655 (20°C)	FCC	1.43
Americium
Antimony	6.4	6.62	630.5	1,440	0.049	8.5 - 10.8	0.045	39.0 (0°C)	R	1.61
Argon	0.62	1.6626 × 10 ⁻³	-189.4	-185.8	.125	...	0.406 × 10 ⁻⁴	...	FCC	1.92
Arsenic	4.1	5.73	814	610	.082	4.7	...	35 (0°C)	R	(1.25)
Barium	1.17	3.5	704	1,640	.068	BCC	2.24
Beryllium	0.0090	-1.85	1,315	2,970	.43	11.6	0.38	5.9 (0°C)	CPH	1.13
Bismuth	.032	9.80	271	1,627	.29	13.4	.019	106.8 (0°C)	R	1.82
Boron	750	2.3	2,000-2,300	2,550	.263	8.3	...	1.8 × 10 ⁻⁴ (0°C)	T-H	0.97
Bromine	6.5	3.12	-7.2	58	.070	O	(1.19)
Cadmium	2,400	8.65	321	765	.055	31.8	0.22	7.51 (18°C)	CPH	1.52
Calcium	0.43	1.55	850	1,440	.149	22	.3	3.43 (0°C)	FCC	1.97
Carbon (Graphite)	.0045	2.22	3,700	4,830	.165	0.6 × 4.3	.057	1,375 (0°C)	H	0.775
Cerium	.70	6.78	780	2,420	.043	75-90 (20°C)	FCC	1.82
Cesium	29.0	1.9	28	690	.052	97	...	18.83 (0°C)	BCC	2.70
Chlorine	31.6	...	-101	-34.7	.116	...	0.172 × 10 ⁻⁴	...	T	(1.07)
Chromium	2.9	7.19	1,890	2,500	.11	6.2	0.16	13 (28°C)	BCC	1.28
Cobalt	34.8	8.8	1,495	2,900	.102	14.2	.165	5.6 (0°C)	CPH	1.25
Columbium (Niobium)	1.1	8.57	2,415065	7.1	...	13.1 (18°C)	BCC	1.47
Copper	3.59	8.96	1,083	2,600	.092	16.5	0.94	1.673 (20°C)	FCC	1.28
Curium
Dysprosium	1,100	8.56	1,400	CPH	1.77
Erbium	166	9.16	>1,440	CPH	1.75
Europium	4,500	5.22	BCC	2.04
Fluorine	<0.010	...	-223	-188.2	0.18
Francium
Gadolinium	44,000	7.95	~1,200	CPH	1.80
Gallium	2.71	5.91	29.78	2,070	0.079	18	...	53.4 (0°C)	OFCC	2.7
Germanium	2.35	5.36	958073	89,000 (0°C)	DC	1.39
Gold	94	19.32	1,063	2,970	.031	14.2	0.71	2.19 (0°C)	FCC	1.44
Hafnium	115	13.36	2,130035	5.9	...	32.7 (0°C)	CPH	1.59
Helium	0.0068	0.1664 × 10 ⁻³	-271.4	-268.9	1.25	...	3.32 × 10 ⁻⁴	...	CPH	...
Holmium	64	8.76	~1,200	CPH	1.76
Hydrogen	0.330	0.08375 × 10 ⁻³	-259.4	-252.7	3.45	...	4.06 × 10 ⁻⁴	...	H	0.46
Illinium
Iodine	190	7.31	156.4	...	0.057	33	0.057	8.37 (0°C)	FCT	1.57
Iridium	6.7	4.93	114	183	.052	93	10.4 × 10 ⁻⁴	1.3 × 10 ¹⁵ (20°C)	O	(1.36)
Iridium	440	22.5	2,454	5,300	.031	6.8	0.14	5.3 (20°C)	FCC	1.35
Iron	2.43	7.87	1,539	2,740	.11	11.7	.18	9.71 (20°C)	BCC	1.28
Krypton	28	3.488 × 10 ⁻³	-157	-152	0.21 × 10 ⁻⁴	...	FCC	1.97
Lanthanum	8.9	6.19	866	4,340	0.048	65-75 (20°C)	CPH	1.87
Lead	0.17	11.34	327.4	1,740	.031	29.3	0.083	20.65 (20°C)	FCC	1.75
Lithium	67	0.53	186	1,370	.79	56	.17	8.55 (0°C)	BCC	1.57
Lutetium	108	9.74	CPH	1.73
Magnesium	0.059	1.74	650	1,120	0.25	26	0.38	4.46 (20°C)	CPH	1.60
Manganese	12.6	7.43	1,245	2,150	.115	22	...	185 (20°C)	Ct	(1.60)
Mercury	380	13.55	-38.87	357	.033	...	0.0201	94.1 (0°C)	R	1.55
Molybdenum	2.4	10.2	2,622	4,804	.061	5.1	.32	5.17 (0°C)	BCC	1.40
Neodymium	44	6.98	820046	70 (20°C)	CPH	1.82
Neon	<2.8	0.8387 × 10 ⁻³	-248.6	-246.0	0.00011	...	FCC	1.60
Neptunium

APPENDIX

Table A.1—(Continued)

Element	Thermal-neutron absorption cross section, barns/atom	Density near 20°C, gm/cm ³	Melting point, °C	Boiling point, °C	Specific heat near 20°C, cal/(gm)(°C)	Coefficient of linear thermal expansion near 20°C, per °C × 10 ⁻⁶	Thermal conductivity near 20°C, cal/(sec)(cm)(°C)	Electrical resistivity, microhm-cm	Crystal structure*	Goldschmidt atomic radius, Å
Nickel	4.5	8.90	1,455	2,730	0.105	13.3	0.22	6.84 (20°C)	FCC	1.25
Nitrogen	1.78	1.1649 × 10 ⁻³	-210.0	-195.8	.247000080	...	H	0.71
Osmium	14.7	22.5	2,700	5,500	.031	4.6	...	9.5 (20°C)	CPH	1.35
Oxygen	<0.0002	1.3318 × 10 ⁻³	-218.8	-183.0	.218	...	0.000059	...	C	0.60
Palladium	8.0	12.0	1,554	4,000	.058	11.8	.17	10.8 (20°C)	FCC	1.37
Phosphorus (yellow)	0.19	1.82	44.1	280	.177	125	...	10 ¹⁷ (11°C)	C	(1.09)
Platinum	8.1	21.45	1,773.5	4,410	.032	8.9	0.17	9.83 (0°C)	FCC	1.38
Plutonium	...	19.6	632	50.3 × 10 ⁻⁶	...	150 (25°C)
Polonium	...	9.51	254	912	...	24.4	...	140	M#	(1.40)
Potassium	1.97	0.86	63	770	0.177	83	0.24	6.15 (0°C)	BCC	2.38
Praseodymium	11.2	6.78	950	3,020	.049	75 (20°C)	CPH	1.83
Protactinium	3,000
Radium	...	5.0	700
Radon	...	4.40	-71	-61.8
Rhenium	84	20	3,170	...	0.033	CPH	1.38
Rhodium	150	12.41	1,968	4,500	.059	12.1	0.21	4.3 (0°C)	FCC	1.34
Rubidium	0.70	1.53	39	680	.080	90	...	12.5 (20°C)	BCC	2.51
Ruthenium	2.46	12.2	2,500	4,900	.057	9.1	...	7.6 (0°C)	CPH	1.34
Samarium	6,500	6.93	>1,300
Scandium	13	2.5	1,400	FCC	1.80
Selenium	11.8	4.81	220	680	0.084	37	H	(1.16)
Silicon	0.13	2.33	1,430	2,300	.162	2.8-7.3	0.20	10 ³ (0°C)	DC	(1.17)
Silver	60	10.49	960.5	2,212	.056	20.6	1.0	1.47 (10°C)	FCC	1.44
Sodium	0.49	0.97	97.7	892	.295	71	0.32	4.2 (0°C)	BCC	1.92
Strontium	1.16	2.6	770	1,380	0.176	23 (20°C)	FCC	2.15
Sulfur (yellow)	0.49	2.07	119.0	444.6	.175	64	6.31 × 10 ⁻⁴	2 × 10 ²³ (20°C)	FCO	(1.04)
Tantalum	21.3	16.6	2,996036	6.5	0.13	12.4 (18°C)	BCC	1.47
Tellurium	4.5	6.24	450	1,390	.047	16.8	.014	2 × 10 ³ (19.6°C)	H	(1.43)
Terbium	44	8.33	>1,400	CPH	1.77
Thallium	3.3	11.85	300	1,460	0.031	28	0.093	18 (0°C)	CPH	1.71
Thorium	...	11.71	1,690	>3,000	.028	11.15	.09	18 (20°C)	FCC	1.80
Thulium	118	9.35	CPH	1.74
Tin	0.65	7.298	231.9	2,270	0.054	23	0.16	11.5 (20°C)	BCT	1.58
Titanium	5.6	4.51	1,690	3,535	.137	8.5	.41	48 (20°C)	CPH	1.47
Tungsten	19.2	19.2	3,395	5,930	.032	4.4	.40	5.5 (20°C)	BCC	1.41
Uranium	...	19.1	1,133	3,900	.028	14.5	.060	25-50 (25°C)	O	(1.38)
Vanadium	4.7	6.1	1,710	3,400	.127	8.3	.07	25 (20°C)	BCC	1.36
Xenon	35	5.495 × 10 ⁻³	-112	-108.0	1.24 × 10 ⁻⁴	...	FCC	2.18
Ytterbium	36	7.01	1,800	FCC	1.93
Yttrium	1.38	5.51	1,475	CPH	1.81
Zinc	1.06	7.133	419.46	906	0.0915	39.7	0.27	5.916 (20°C)	CPH	1.37
Zirconium	0.18	6.5	1,845069	5	.057	41.0 (0°C)	CPH	1.80

* FCC = Face-centered cubic; R = Rhombohedral; BCC = Body-centered cubic; CPH = Close-packed hexagonal; O = Orthorhombic; H = Hexagonal; T = Tetragonal; DC = Diamond cubic; OFCO = One-face-centered orthorhombic; M = Monoclinic; BCT = Body-centered tetragonal

† Figures in parentheses are one-half the smallest interatomic distances

‡ Complex cubic

§ Probably monoclinic with $\beta = 92^\circ$

Table A.2—Thermal-neutron Absorption Cross-section of the Elements Arranged in Order of Atomic Number

(Neutron Cross Sections, AECU 2040)

Z	Element	Barns/atom		Cm ² /gram	Z	Element	Barns/atom		Cm ² /gram
		Value	Uncertainty				Value	Uncertainty	
1	H	0.330	±0.007	0.198	42	Mo	2.4	±0.2	0.0151
2	He	.006800102	43	Tc
3	Li	67	±2	5.8	44	Ru	2.46	±0.12	0.0146
4	Be	0.0090	±0.0005	0.00060	45	Rh	150	±7	.88
5	B	750	±10	42	46	Pd	8.0	±1.5	.045
6	C	0.0045	...	0.00022	47	Ag	60	±3	.34
7	N	1.78	±0.05	.076	48	Cd	2400	±200	12.9
8	O	<0.0002	...	<.0000075	49	In	190	10	1.00
9	F	<.010	...	<.00032	50	Sn	0.65	±0.05	0.0033
10	Ne	<.8	...	<.084	51	Sb	6.4	±1.0	.032
11	Na	0.49	±0.02	.0128	52	Te	4.5	±0.2	.021
12	Mg	.059	±.004	.00146	53	I	6.7	±.6	.032
13	Al	.215	±.008	.0048	54	Xe	35	±5	.161
14	Si	.13	±.03	.0028	55	Cs	29 0	±1.5	.132
15	P	.19	±.03	.0037	56	Ba	1.17	±0.10	.0051
16	S	.49	±.02	.0092	57	La	8.9	±.3	.039
17	Cl	31.6	±1	.54	58	Ce	0.70	±.08	.0030
18	A	0.62	±0.04	.0094	59	Pr	11.2	±.6	.048
19	K	1.97	±.06	.030	60	Nd	44	±2.0	.183
20	Ca	0.43	±.02	.0065	61	Pm
21	Sc	13	±2	.173	62	Sm	6500	±1000	26
22	Ti	5.6	±0.4	.070	63	Eu	4500	±500	17.9
23	V	4.7	±.2	.055	64	Gd	44000	±2000	169
24	Cr	2.9	±.1	.033	65	Tb	44	±4	0.166
25	Mn	12.6	±.6	.139	66	Dy	1100	±150	4.1
26	Fe	2.43	±.08	.026	67	Ho	64	±3	0.23
27	Co	34.8	±2.0	.35	68	Er	166	±16	.60
28	Ni	4.5	±0.2	.046	69	Tm	118	±6	.42
29	Cu	3.59	±.12	.034	70	Yb	36	±4	.125
30	Zn	1.06	±.05	.0098	71	Lu	108	±5	.37
31	Ga	2.71	±.12	.023	72	Hf	115	±15	.39
32	Ge	2.35	±.20	.0195	73	Ta	21.3	±1.0	.071
33	As	4.1	±.2	.033	74	W	19.2	±1.0	.063
34	Se	11.8	±.4	.090	75	Re	84	±4	.27
35	Br	6.5	±.5	.049	76	Os	14.7	±0.7	.047
36	Kr	28	±5	.20	77	Ir	440	±20	1.37
37	Rb	0.70	±0.07	.0049	78	Pt	8.1	±0.4	0.025
38	Sr	1.16	±.06	.0080	79	Au	94	±1	.29
39	Y	1.38	±.14	.0094	80	Hg	380	±20	1.14
40	Zr	0.18	±.02	.00119	81	Tl	3.3	±0.5	0.0098
41	Nb	1.1	±.1	.0071	82	Pb	0.17	±.01	.00050
					83	Bi	.032	±.003	.000092

APPENDIX

Table A.3—Thermal-neutron Absorption Cross-section of the Elements Arranged in
Order of Increasing Cross-section
(Neutron Cross Sections, AECU 2040)

Element	Z	Cm ² /gram	Barns/atom	Element	Z	Cm ² /gram	Barns/atom
O	8	0.0000075	<0.0002	Ni	28	0.046	4.5
Bi	83	.000092	.032	Os	76	.047	14.7
C	6	.00022	.0045	Pr	59	.048	11.2
F	9	.00032	.010	Br	35	.049	6.5
Pb	82	.00050	.17	V	23	.055	4.7
Be	4	.00060	.0090	W	74	.063	19.2
He	2	.00102	.0068	Tl	22	.070	5.6
Zr	40	.00119	.18	Ta	73	.071	21.3
Mg	12	.00146	.059	N	7	.076	1.78
Si	14	.0028	.13	Ne	10	.084	<2.8
Ce	58	.0030	.70	Se	34	.090	11.8
Sn	50	.0033	.65	Yb	70	.125	36
P	15	.0037	.19	Cs	55	.132	29.0
Al	13	.0048	.215	Mn	25	.139	12.6
Rb	37	.0049	.70	Xe	54	.161	35
Ba	56	.0051	1.17	Tb	65	.166	44
Ca	20	.0065	0.43	Sc	21	.173	13
Nb	41	.0071	1.1	Nd	60	.183	44
Sr	38	.0080	1.16	H	1	.198	0.330
S	16	.0092	0.49	Kr	36	.20	28
Y	39	.0094	1.38	Ho	67	.23	64
A	18	.0094	0.62	Re	75	.27	84
Zn	30	.0098	1.06	Au	79	.29	94
Tl	81	.0098	3.3	Ag	47	.34	60
Na	11	.0128	0.49	Co	27	.35	34.8
Ru	44	.0146	2.46	Lu	71	.37	108
Mo	42	.0151	2.4	Hf	72	.39	115
Ge	32	.0195	2.35	Tm	69	.42	118
Te	52	.021	4.5	Cl	17	.54	31.6
Ga	31	.023	2.71	Er	68	.60	166
Pt	78	.025	8.1	Rh	45	.88	150
Fe	26	.026	2.43	In	49	1.00	190
K	19	.030	1.97	Hg	80	1.14	380
I	53	.032	6.7	Ir	77	1.37	440
Sb	51	.032	6.4	Dy	66	4.1	1100
Cr	24	.033	2.9	Li	3	5.8	67
As	33	.033	4.1	Cd	48	12.8	2400
Cu	29	.034	3.59	Eu	63	17.9	4500
La	57	.039	8.9	Sm	62	26	6500
Pd	46	.045	8.0	B	5	42	750
				Gd	64	169	44000

MATERIALS

Table A.4—Temperature Conversions*
(ASM Data Sheet, Number 9)

-459.4 to 0				0 to 100				100 to 1000				1000 to 2000				2000 to 3000									
C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F								
-273	-459.4	-17.8	0	32	10.0	50	122.0	38	100	212	260	500	932	538	1000	1832	816	1500	2732	1093	2000	3632	1371	2500	4532
-268	-450	-17.2	1	33.8	10.6	51	123.8	43	110	230	266	510	950	543	1010	1850	821	1510	2750	1099	2010	3650	1377	2510	4550
-262	-440	-16.7	2	35.6	11.1	52	125.6	49	120	248	271	520	968	545	1020	1868	827	1520	2768	1104	2020	3668	1382	2520	4568
-257	-430	-16.1	3	37.4	11.7	53	127.4	54	130	266	277	530	986	554	1030	1886	832	1530	2786	1110	2030	3686	1388	2530	4586
-251	-420	-15.6	4	39.2	12.2	54	129.2	60	140	284	282	540	1004	560	1040	1904	838	1540	2804	1116	2040	3704	1393	2540	4604
-246	-410	-15.0	5	41.0	12.8	55	131.0	66	150	302	288	550	1022	566	1050	1922	843	1550	2822	1121	2050	3722	1399	2550	4622
-240	-400	-14.4	6	42.8	13.3	56	132.8	71	160	320	293	560	1040	571	1060	1940	849	1560	2840	1127	2060	3740	1404	2560	4640
-234	-390	-13.9	7	44.6	13.9	57	134.6	77	170	338	299	570	1058	577	1070	1958	854	1570	2858	1132	2070	3758	1410	2570	4658
-229	-380	-13.3	8	46.4	14.4	58	136.4	82	180	356	304	580	1076	582	1080	1976	860	1580	2876	1138	2080	3776	1416	2580	4676
-223	-370	-12.8	9	48.2	15.0	59	138.2	88	190	374	310	590	1094	588	1090	1994	866	1590	2894	1143	2090	3794	1421	2590	4694
-218	-360	-12.2	10	50.0	15.6	60	140.0	93	200	392	316	600	1112	593	1100	2012	871	1600	2912	1149	2100	3812	1427	2600	4712
-212	-350	-11.7	11	51.8	16.1	61	141.8	99	210	410	321	610	1130	599	1110	2030	877	1610	2930	1154	2110	3830	1432	2610	4730
-207	-340	-11.1	12	53.6	16.7	62	143.6	100	212	413.6	327	620	1148	604	1120	2048	882	1620	2948	1160	2120	3848	1438	2620	4748
-201	-330	-10.6	13	55.4	17.2	63	145.4	104	220	428	332	630	1166	610	1130	2066	888	1630	2966	1166	2130	3866	1443	2630	4766
-196	-320	-10.0	14	57.2	17.8	64	147.2	110	230	446	338	640	1184	616	1140	2084	893	1640	2984	1171	2140	3884	1449	2640	4784
-190	-310	-9.4	15	59.0	18.3	65	149.0	116	240	464	343	650	1202	621	1150	2102	899	1650	3002	1177	2150	3902	1454	2650	4802
-184	-300	-8.9	16	60.8	18.9	66	150.8	121	250	482	349	660	1220	627	1160	2120	904	1660	3020	1182	2160	3920	1460	2660	4820
-179	-290	-8.3	17	62.6	19.4	67	152.6	127	260	500	354	670	1238	632	1170	2138	910	1670	3038	1188	2170	3938	1466	2670	4838
-173	-280	-7.8	18	64.4	20.0	68	154.4	132	270	518	360	680	1256	638	1180	2156	916	1680	3056	1193	2180	3956	1471	2680	4856
-169	-273	-7.2	19	66.2	20.6	69	156.2	138	280	536	366	690	1274	643	1190	2174	921	1690	3074	1199	2190	3974	1477	2690	4874
-168	-270	-6.7	20	68.0	21.1	70	158.0	143	290	554	371	700	1292	649	1200	2192	927	1700	3092	1204	2200	3992	1482	2700	4892
-162	-260	-6.1	21	69.8	21.7	71	159.8	149	300	572	377	710	1310	654	1210	2210	932	1710	3110	1210	2210	4010	1488	2710	4910
-157	-250	-5.6	22	71.6	22.2	72	161.6	154	310	590	382	720	1328	660	1220	2228	938	1720	3128	1216	2220	4028	1493	2720	4928
-151	-240	-5.0	23	73.4	22.8	73	163.4	160	320	608	388	730	1346	666	1230	2246	943	1730	3146	1221	2230	4046	1499	2730	4946
-146	-230	-4.4	24	75.2	23.3	74	165.2	166	330	626	393	740	1364	671	1240	2264	949	1740	3164	1227	2240	4064	1504	2740	4964

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-140	-220	-364	-3.9	25	77.0	23.9	75	167.0	171	340	644	399	750	1382	677	1250	2282	954	1750	3182	1232	22.0	4082	1510	2750	4982
-134	-210	-346	-3.3	26	78.8	24.4	76	168.8	177	350	662	404	760	1400	682	1260	2300	960	1760	3200	1238	2260	4100	1516	2760	5000
-129	-200	-328	-2.8	27	80.6	25.0	77	170.6	182	360	680	410	770	1418	688	1270	2318	966	1770	3218	1243	2270	4118	1521	2770	5018
-123	-190	-310	-2.2	28	82.4	25.6	78	172.4	188	370	698	416	780	1436	693	1280	2336	971	1780	3236	1249	2280	4136	1527	2780	5036
-118	-180	-292	-1.7	29	84.2	26.1	79	174.2	193	380	716	421	790	1454	699	1290	2354	977	1790	3254	1254	2290	4154	1532	2790	5054
-112	-170	-274	-1.1	30	86.0	26.7	80	176.0	199	390	734	427	800	1472	704	1300	2372	982	1800	3272	1260	2300	4172	1538	2800	5072
-107	-160	-256	-0.6	31	87.8	27.2	81	177.8	204	400	752	432	810	1490	710	1310	2390	988	1810	3290	1266	2310	4190	1543	2810	5090
-101	-150	-238	0.0	32	89.6	27.8	82	179.6	210	410	770	438	820	1508	716	1320	2408	993	1820	3308	1271	2320	4208	1549	2820	5108
-96	-140	-220	0.6	33	91.4	28.3	83	181.4	216	420	788	443	830	1526	721	1330	2426	999	1830	3326	1277	2330	4226	1554	2830	5126
-90	-130	-202	1.1	34	93.2	28.9	84	183.2	221	430	806	449	840	1544	727	1340	2444	1004	1840	3344	1282	2340	4244	1560	2840	5144
-84	-120	-184	1.7	35	95.0	29.4	85	185.0	227	440	824	454	850	1562	732	1350	2462	1010	1850	3362	1288	2350	4262	1566	2850	5162
-79	-110	-166	2.2	36	96.8	30.0	86	186.8	232	450	842	460	860	1580	738	1360	2480	1016	1860	3380	1293	2360	4280	1571	2860	5180
-73	-100	-148	2.8	37	98.6	30.6	87	188.6	238	460	860	466	870	1598	743	1370	2498	1021	1870	3398	1299	2370	4298	1577	2870	5198
-68	-90	-130	3.3	38	100.4	31.1	88	190.4	243	470	878	471	880	1616	749	1380	2516	1027	1880	3416	1304	2380	4316	1582	2880	5216
-62	-80	-112	3.9	39	102.2	31.7	89	192.2	249	480	896	477	890	1634	754	1390	2534	1032	1890	3434	1310	2390	4334	1588	2890	5231
-57	-70	-94	4.4	40	104.0	32.2	90	194.0	254	490	914	482	900	1652	760	1400	2552	1038	1900	3452	1316	2400	4352	1593	2900	5252
-51	-60	-76	5.0	41	105.8	32.8	91	195.8				488	910	1670	766	1410	2570	1043	1910	3470	1321	2410	4370	1599	2910	5270
-46	-50	-58	5.6	42	107.6	33.3	92	197.6				493	920	1688	771	1420	2588	1049	1920	3488	1327	2420	4388	1604	2920	5288
-40	-40	-40	6.1	43	109.4	33.9	93	199.4				499	930	1706	777	1430	2606	1054	1930	3506	1332	2430	4406	1610	2930	5306
-34	-30	-22	6.7	44	111.2	34.4	94	201.2				504	940	1724	782	1440	2624	1060	1940	3524	1338	2440	4424	1616	2940	5324
-29	-20	-4	7.2	45	113.0	35.0	95	203.0				510	950	1742	788	1450	2642	1066	1950	3542	1343	2450	4442	1621	2950	5342
-23	-10	14	7.8	46	114.8	35.6	96	204.8				516	960	1760	793	1460	2660	1071	1960	3560	1349	2460	4460	1627	2960	5360
-17.8	0	32	8.3	47	116.6	36.1	97	206.6				521	970	1778	799	1470	2678	1077	1970	3578	1354	2470	4478	1632	2970	5378
			8.9	48	118.4	36.7	98	208.4				527	980	1796	804	1480	2696	1082	1980	3596	1360	2480	4496	1638	2980	5396
			9.4	49	120.2	37.2	99	210.2				532	990	1814	810	1490	2714	1088	1990	3614	1366	2490	4514	1643	2990	5414
			37.8	100	212.0							538	1000	1832				1093	2000	3632				1649	3000	5432

*Albert Sauveur type of table. Look up reading in middle column; if in degrees centigrade, read fahrenheit equivalent in right-hand column; if in degrees fahrenheit, read centigrade equivalent in left-hand column

Table A.5 — Some Engineering Conversion Factors
(Manual of Pile Engineering, CF-51-8-10, Dec. 28, 1951)

Multiply	By	To obtain
Btu	778.2	ft-lb
Btu	107.6	kg-meters
Btu	1055	joules
Btu	0.2520	kg-cal
Btu	3.930×10^{-4}	hp-hr
Btu	2.930×10^{-4}	kw-hr
Btu	0.5556	P. C. U.*
Btu/ft ³	8.90	kg-cal/m ³
Btu/hr	3.927×10^{-4}	hp
Btu/(hr)(ft ²)	2.712	kg-cal/(hr)(m ²)
Btu/(hr)(ft ²)(°F)	4.882	kg-cal/(hr)(m ²)(°C)
Btu/(hr)(ft ²)(°F)	1.0	P.C.U.*/(hr)(ft ²)(°C)
Btu/(hr)(ft ²)(°F)	1.356×10^{-4}	gm-cal/(cm ²)(sec)(°C)
Btu/(hr)(ft ²)(°F)	5.68×10^{-4}	watts/(cm ²)(°C)
Btu/(hr)(ft ²)(°F)	2.035×10^{-3}	watts/(in. ²)(°F)
Btu/(hr)(ft ²)(°F)/in.	12.4	kg-cal/(hr)(m ²)(°C)/cm
Btu/(hr)(ft ²)(°F)/in.	3.445×10^{-4}	gm-cal/(cm)(sec)(°C)
Btu/(hr)(ft)(°F)	4.13×10^{-3}	gm-cal/(cm)(sec)(°C)
Btu/(hr)(ft)(°F)	0.0173	watts/(cm)(°C)
Btu/(hr)(ft)(°F)	14.88	gm-cal/(hr)(cm)(°C)
Btu/min	12.97	ft-lb/sec
Btu/min	0.02358	hp
Btu/min	.01758	kw
Btu/lb	.556	gm-cal/gm
Btu/lb-mol	.556	gm-cal/gm-mol
Btu/(lb)(°F)	1.0	gm-cal/(gm)(°C)
Btu/sec	778.2	ft-lb/sec
Btu/sec	1.4147	hp
Btu/sec	1.0549	kw
Btu/sec	107.6	gm-cal/cm ²
Btu/ft ²	0.2712	kg-cal/m ²
Btu/ft ²	2.712	kg-cal/sq meter
degrees/sec	2.778×10^{-3}	rev/sec
degrees/sec	0.1667	rpm
dynes	1.02×10^{-3}	gm
dynes/cm	6.85×10^{-6}	lb/ft
ergs	1.0×10^{-7}	joules
ft/min	0.508	cm/sec
ft-lb	3.239×10^{-4}	kg-cal
ft-lb/min	2.26×10^{-6}	kw
ft-lb/sec	0.0771	Btu/min
ft-lb/sec	.01943	kg-cal/min
gm	980.7	dynes
gm	2.205×10^{-3}	lb
gm-mol gas	2.24×10^4	cm ³ gas (0°C and 760 mm)
gm-cal	3.968×10^{-3}	Btu
gm-cal	4.186	joules
gm-cal/gm	1.8	Btu/lb
gm-cal/gm-mol	1.8	Btu/lb-mol
gm-cal/(gm)(°C)	1.0	Btu/(lb)(°F)
gm-cal/cm ²	3.687	Btu/ft ²
gm-cal/cm	1.452	(Btu/ft ²)/in.
gm-cal/(cm ²)(sec)(°C)	7.373×10^3	Btu/(hr)(ft ²)(°F)

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Table A.5—(Continued)

Multiply	By	To obtain
gm-cal/(cm)(sec)(°C)	2.903×10^3	Btu/(hr)(ft ²)(°F)/in.
gm-cm	9.294×10^{-8}	Btu
gm-cm	980.6	ergs
gm-cm	7.233×10^{-6}	ft-lb
gm-cm	2.342×10^{-8}	kg-cal
gm/cm	5.60×10^{-3}	lb/in.
gm/cm ³	1.0	specific gravity at 4°C
gm/cm ³	62.43	lb/ft ³
gm/cm ²	0.07355	cm Hg
gm/cm ²	10	kg/m ²
gm/cm ²	0.394	in. of water
gm/cm ²	.03281	ft of water
gm/cm ²	9.678×10^{-4}	atm
gm/cm ²	0.01422	lb/in. ²
gm/cm ²	2.048	lb/ft ²
hp	42.41	Btu/min
hp	3.3×10^4	ft-lb/min
hp	550	ft-lb/sec
hp	10.7	kg-cal/min
hp	0.7457	kw
in./°F	4.572	cm/°C
joules	1×10^7	ergs
joules	$2.39 \times 10^{-4} \times 10^3$	kg-cal
joules	0.102	kg-meters
joules	2.778×10^{-4}	watt-hr
joules	5.265×10^{-4}	P. C. U.*
joules	0.7376	ft-lb
joules	9.486×10^{-4}	Btu
joules/gm	0.4305	Btu/lb
joules/(gm)(°C)	.2389	Btu/(lb)(°F)
joules/(gm)(°C)	2.2389	gm-cal/(gm)(°C)
kg-cal/(hr)(m ²)	0.3685	Btu/(hr)(ft ²)
kg-cal/(hr)(m ²)(°C)	.2048	Btu/(hr)(ft ²)(°F)
kg-cal/min	51.43	ft-lb/sec
kg-cal/min	0.09351	hp
kg-cal/min	.06972	kw
watts	.05692	Btu/min
watts	1×10^7	ergs/sec
watts	44.26	ft-lb/min
watts	0.7376	ft-lb/sec
watts	1.341×10^{-3}	hp
watts	0.01434	kg-cal/min
watts	1.0×10^{-3}	kw
watt-hr	3.413	Btu
watt-hr	2.655×10^{-3}	ft-lb
watt-hr	1.341×10^{-3}	hp-hr
watt-hr	0.8605	kg-cal
watt-hr	367.1	kg-meter
week	168	hr
week	1.008×10^4	min
week	6.048×10^5	sec
yr (common)	8.76×10^3	hr

*Pound-centigrade unit

Fig. A.1—A Metallurgist's Periodic Table.

Table A. 6—Glossary of Selected Metallurgical Terms
(Adapted from Glossary of Nuclear Energy Terms, ASME, 1950)

Age Hardening (precipitation hardening)	Deformation Bands
A process of hardening an alloy in supersaturated solid solution, usually produced by rapid cooling from an elevated temperature by heating or holding at a lower temperature. Hardening generally occurs by a precipitation reaction from the solid solution or by a pre-precipitation arrangement of the atoms such that the strains induced are sufficient to cause hardening.	Regions within a metal crystal which have assumed different orientations as a result of slip.
Annealing	Dendrite
A process involving heating and cooling, usually applied to induce softening; the process of heating, whereby the properties changed by radiation are partially or wholly restored.	A crystal, usually produced by solidification of liquid, and characterized by a treelike structure with many branches.
Biscuit (derby)	Dislocation
The solid metallic product which results from reduction of a metallic compound by an active metal in a bomb or furnace.	A type of lattice imperfection whose existence in metals is postulated in order to account for the phenomena of crystal growth and of slip particularly for the low value of shear stress required to initiate slip.
Charpy Test	Edge-cracks
A type of impact test in which a notched specimen is supported freely at both ends and broken by the impact of a falling pendulum.	The cracks that occur at the edges of metal sheets during rolling.
Cladding	Embrittlement
A process of coating one metal with another, which usually consists of bringing the carefully prepared surfaces of the two metals in contact, and rolling, extruding, drawing, or swaging the composite until a bond is produced.	An increase in the susceptibility of a metal to fracture under stress caused by the introduction of gas or other foreign atoms, by segregation of brittle constituents, by internal oxidation, or by certain types of corrosion.
Cold Pressing	Eutectic
The process of compressing metal or other powders in a die at room temperature to form a compact. Cold pressing is usually followed by sintering at elevated temperatures.	The isothermal, constant composition transformation of a liquid to more than one solid phase upon cooling; the liquid alloy composition which undergoes the eutectic transformation and possesses the lowest freezing point in its range of composition; the solid alloy, containing more than one phase, which results from the eutectic transformation.
Creep	Fatigue
The plastic deformation of metals that occurs with time upon application of load. Under constant load, the rate of deformation is large at the outset (initial or primary creep) and later becomes substantially constant (second stage or secondary creep). Eventually the metal may deform rapidly once more and may ultimately rupture (third stage or tertiary creep). The slope of the elongation-time curve during the second stage is usually called the creep rate.	The tendency for a metal to fracture under repeated stressing considerably below the ultimate tensile strength. The fatigue limit or endurance limit of a metal or alloy is that stress below which failure will presumably not occur in an infinite number of cycles. When such a limit does not exist, the term is often applied to the stress causing fracture in a specified large number of cycles. The endurance ratio is the endurance limit divided by the tensile strength. For most carbon and alloy steels this ratio is approximately 0.5, while for nonferrous alloys it may be less than 0.25 or greater than 0.5.

Table A.6—(Continued)

Hardness	A property defining resistance to deformation, whose value depends upon the method of measurement.	Pickle	The removal of metallic compounds, usually oxides, from the surface of a metal by chemical or electrochemical means.
Impact Strength	A property which is measured by the energy absorbed by a metal specimen when it is fractured at high velocity.	Pipe	A cavity, usually along the center line of an ingot, created by the contraction which accompanies solidification.
Izod Test	An impact test in which a standard notched specimen supported at one end as a cantilever beam is broken by the impact of a moving pendulum.	Recovery (in metallurgy)	In physical metallurgy, a process which usually precedes recrystallization when cold-worked metals are annealed; residual stresses are partially relieved, but strength, ductility, and grain structure remain substantially unchanged; recovery is probably associated with elastic adjustments in individual grains. In extractive metallurgy, the fraction of the valuable component which is obtained from an ore by processing.
Lattice Parameter (lattice spacing, lattice constants)	The lengths of the edges of the unit cell in a crystal.	Recrystallization	A process which occurs upon annealing cold-worked metals in which the original stressed and distorted grains are replaced by stress-free grains. The grain size resulting from recrystallization may be increased by further annealing to cause grain growth.
Metastable Equilibrium	A condition of pseudoequilibrium in which the free energy of a system is at a minimum with respect to infinitesimal changes but not with respect to major changes.	Scalping	The removal of the surface layers of metal ingots, billets, or slabs by machining or other means prior to fabrication.
Modulus of Elasticity	The ratio of stress to strain within the elastic range. When the modulus of elasticity is determined from the slope of the stress-strain curve in a tension or compression test, it is often called Young's modulus. The modulus of elasticity in shear is termed the modulus of rigidity. For metals, the shear modulus is approximately 0.4 the modulus of elasticity in tension.	Sintering	The process of bonding metal or other powders by heating to form a strong cohesive body. The powders are usually first cold-pressed into the desired shape. Sintering is usually accompanied by a considerable reduction in volume.
Peritectic	A type of phase change in which in two-component systems a liquid melt and a solid phase interact upon cooling to produce a second solid phase of composition intermediate between the two.	Stress-to-rupture	A type of high-temperature test in which the stress required to cause rupture in a stated time is determined. The data from these tests are usually reported as stresses to produce rupture in 10, 100, and 1000 hr, accompanied by the elongations at rupture.
Phase	A portion of a system which is homogeneous to the instruments of detection, or whose parts are all in the same thermodynamic state.	Widmanstätten Structure	A structure in which a geometrical metallographic pattern is produced by the generation of a new phase within the body of the parent phase. The shape of the particles of the new phase, and their crystallographic orientations are both related to the orientation of the parent crystal.
Phase Diagram (constitutional diagram, equilibrium diagram)	A representation, either graphical or by means of a model, of the equilibrium temperature, pressure, and composition limits of the phase regions of a system. In metallic systems, the pressure is usually considered constant, and a binary system may be represented in two dimensions with temperature usually the ordinate and composition the abscissa.		

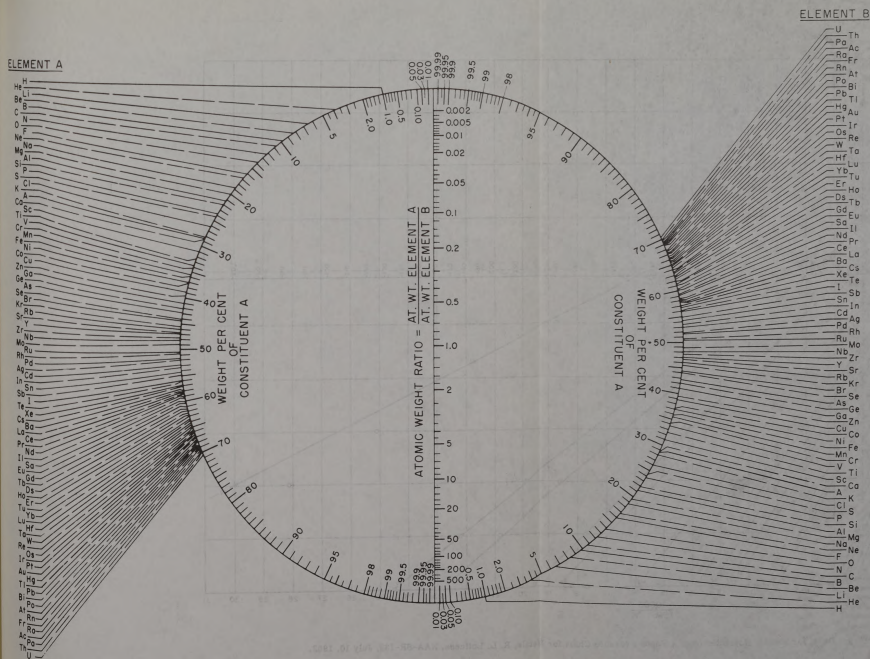


Fig. A.2—A Nomograph for Interconversion of Weight- and Atomic-percent. Prepared by Battelle Memorial Institute, Sept. 1, 1952.

INSTRUCTIONS FOR USE OF FIG. A.2

Use of Chart

1. Join points corresponding to Elements A and B by a straight line.
2. Note where this line cuts the ratio scale.
3. A straight line through this point on the ratio scale joins the corresponding weight and atomic percentages of Element A on the circle.

Example

Find the atomic-percent of copper in a copper-lead alloy containing 75 weight-percent copper.

Steps 1 and 2 give an atomic weight ratio of slightly over 0.3. Step 3 gives 90.7 atomic-percent copper.

Other Applications

This nomograph can also be used for determining the atomic composition of salts or the molecular concentrations in binary mixtures of any compounds of known molecular weight. In the latter case, one would simply compute the ratio of molecular weights, locate this point, and then draw a line through this point to join corresponding weight and mole percentages. In fact, this chart can be used for any conversions which follow the same type of formula as relates atomic- and weight-percent. For instance, volume and weight percentages can be interconverted by calling the center scale specific-gravity ratio instead of atomic weight ratio.

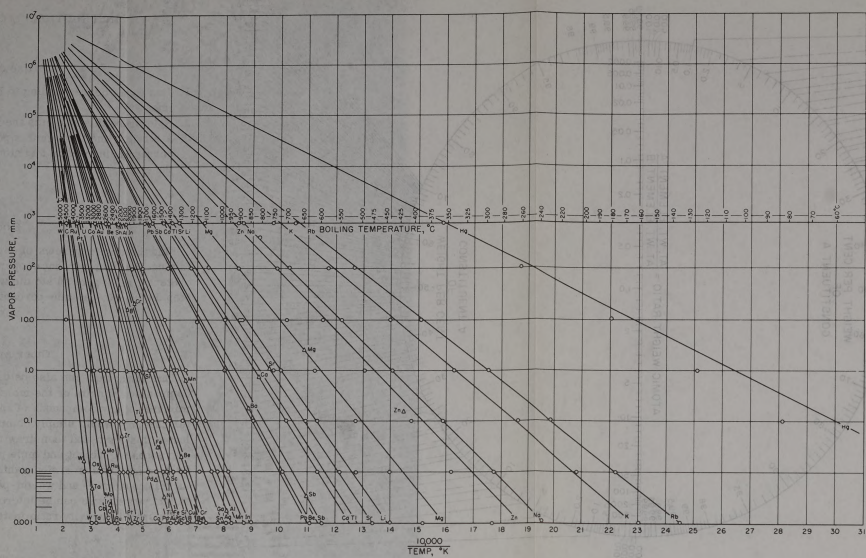


Fig. A.3—A Vapor Pressure Chart for Metals. Reprinted from A Vapor Pressure Chart for Metals, R. L. Loftness, NAA-SR-132, July 10, 1952.

APPENDIX

SELECTED READING LIST*

THE BEHAVIOR OF ENGINEERING MATERIALS, H. W. Gillett, John Wiley and Sons, New York City, 395 pp, 1951.

METALS REFERENCE BOOK, C. J. Smithells, Interscience Publishers, Inc., New York City, 735 pp, 1949.

THE CORROSION HANDBOOK, H. H. Uhlig, John Wiley and Sons, New York City, 1188 pp, 1948.

METALS HANDBOOK, American Society for Metals, 1948 Edition, Cleveland, Ohio.

*A list prepared to assist the reactor engineer in obtaining some background on the general subject of materials.

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